

This Page Is Inserted by IFW Operations  
and is not a part of the Official Record

## **BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning documents *will not* correct images,  
please do not report the images to the  
Image Problem Mailbox.**



**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LK	Sri Lanka	SN	Senegal
CN	China	LU	Luxembourg	TD	Chad
CS	Czechoslovakia	LV	Latvia	TG	Togo
CZ	Czech Republic	MC	Monaco	TJ	Tajikistan
DE	Germany	MD	Republic of Moldova	TT	Trinidad and Tobago
DK	Denmark	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	US	United States of America
FI	Finland	MN	Mongolia	UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

MEDIUM CONSISTENCY OZONE BRIGHTENING  
OF HIGH CONSISTENCY OZONE BLEACHED PULP

Cross-Reference to Related Applications

This application is a continuation-in-part of  
5 application serial no. 07/896,481 filed September 6,  
1992, which is a continuation of application serial no.  
07/525,808 filed May 17, 1990, now abandoned.

Field of the Invention

10 The invention relates to methods of bleaching  
lignocellulosic materials and more particularly, to a  
later brightening stage conducted using a medium  
consistency ozone stage on wood pulp which has been  
partially bleached with a high consistency ozone stage.

15

Background of the Invention

The processing of chemical and semi-chemical  
cellulosic pulps in the manufacture of various grades of  
paper and paper products generally requires that such  
20 pulps be subjected to several successive bleaching  
treatments. These bleaching treatments are optionally  
interspersed with various washing, dilution, extraction  
and/or concentration stages in order to arrive at a final  
product having a desired lignin content and a desired  
25 brightness.

It has been conventional for many years to delignify  
and bleach wood pulp with elemental chlorine ("C") and/or  
chlorine-containing compounds such as chlorine dioxide  
("D"). This process is described, for example, in U.S.  
30 patents No. 1,957,937 to Campbell et al.; 2,975,169 to  
Cranford et al., and 3,462,344 to Kindron et al., as well  
as in the Handbook For Pulp and Paper Technologists -  
Chapter 11: Bleaching (§11.3), TAPPI, USA.

However, although compounds such as those described  
35 above have proven to be effective bleaching agents, they

suffer from several deficiencies, e.g., they are difficult to handle and they cause corrosion of the processing equipment within the mill. In addition, concern about the possible environmental effects of disposing of chlorine-containing effluents from pulp bleaching mills by sewerage of these effluents has led to significant changes in government requirements and permits for such mills. These new rules mandate more stringent standards for the handling of such effluents. Moreover, the recycle of these effluents is not in itself a satisfactory answer since the build-up of chlorides within the mill over time precludes the operation of such a closed system without employing recovery techniques requiring extensive, and therefore expensive, modifications.

In an effort to overcome these disadvantages, those working in this field have extensively examined numerous alternative bleaching processes designed to reduce or eliminate the use of elemental chlorine and chlorine-containing compounds from multi-stage bleaching processes for lignocellulosic pulps. These alternative processes utilize, for example, various combinations of oxygen ("O"), ozone ("Z"), alkaline extraction ("E") and peroxides ("P"), to name but a few of the chemicals used. Complicating these efforts, however, is the requirement that high levels of pulp brightness are necessary for many of the applications for which such pulp is to be used. The prior art processes which utilize these materials in various combinations are, however, often unable to achieve these high pulp brightness levels without an unacceptable loss in pulp strength, as evidenced by a corresponding decrease in viscosity of the pulp product.

One commercially successful chlorine-free bleaching sequence is disclosed in U.S. Patent No. 5,164,043. This patent discloses a multi-stage process for delignifying

and bleaching a lignocellulosic material. Initially, a pulp is formed from the lignocellulosic material by Kraft pulping, Kraft AQ pulping or extended delignification. The pulp is then partially delignified with oxygen preferably according to a modified alkaline addition  
5 technique where the alkaline material is substantially uniformly combined with the pulp at low consistency prior to removing pressate and forming a high consistency pulp which is then contacted with the oxygen. Next, the partially delignified pulp is treated with a chelating  
10 agent and an acid so that the pH is in the range of about 1 to 4, and the pulp is then further delignified with ozone. Preferably, the ozone stage is conducted on high consistency pulp utilizing a dynamic reactor which  
15 turbulently mixes the pulp with the ozone gas so that substantially all pulp particles are exposed to the ozone gas for reaction therewith. This enables the pulp to be substantially uniformly bleached, thus forming an intermediate pulp. When desired, this intermediate pulp can be further processed by an alkaline extraction step  
20 followed by a brightening step which uses chlorine dioxide or a peroxide compound. The intermediate pulp has a brightness of between about 35 and 80 GEB whereas the final brightened pulp has a brightness of between about 70 and 90 GEB.

25 While this patented process is highly effective, improvements in bleaching the pulp to high brightnesses are desirable for a variety of reasons, and the present invention provides one such improvement.

### 30 Summary of the Invention

The process of the present invention provides novel combinations of delignification and bleaching steps which eliminate the problems encountered in the prior art by increasing the efficiency and reducing the cost and  
35 duration of pulp bleaching. The multi-stage process of

the invention also eliminates the use of elemental chlorine and/or chlorine-containing bleaching agents, thus substantially reducing or eliminating pollution of the environment while optimizing the physical properties of the resultant pulp product in an energy efficient, cost effective manner. The present process is operable on virtually all wood species, including the difficult-to-bleach southern U.S. softwoods, as well as the more readily bleached hardwoods.

The present processes include several stages, i.e., a pulping stage, an oxygen delignification stage and an ozone delignification/bleaching stage which together comprise what will be referred to herein as the bulk delignification portion of the process. In addition, these processes further comprise various brightening sequences which follow directly upon completion of the ozone treatment. Thus, the process provides pulp having GE brightness values comparable to those in the prior art without sacrificing pulp strength.

The present processes reduce the amount of lignin as much as is practical in the delignification portion of the process (as evidenced by a corresponding decrease in the K No. of the pulp) without a concomitant substantial (and therefore unacceptable) decrease in pulp strength. This, in turn, ensures that the viscosity of the pulp exiting the ozone delignification bleaching stage remains sufficiently high to permit the pulp to withstand the effects of the subsequent bleaching treatments, thus enabling the formation of a final bleached pulp product having sufficient strength and GE brightness ("GEB") for its intended application.

Following the ozone delignification stage, the substantially delignified pulp has a GEB of from about 40-80 and preferably at least about 59. Generally, for softwoods, the target brightness after the ozone stage is

about 48-70, while for hardwoods, it can be as high as 60-80.

If desired, an extraction stage may be conducted prior to further brightening of the pulp. The alkaline extraction step is typically conducted by contacting the pulp with a solution of an alkaline material for a sufficient time and at a sufficient temperature to solubilize a substantial portion of any lignin which was degraded in the previous ozone stage but was not removed from the pulp. If an extraction stage is used, it may be augmented with either oxygen, peroxide or oxygen and peroxide, if desired. It is also possible and advantageous to use additives such as sodium borohydride, formamidine sulfinic acid or sodium hydrosulfite to prevent loss of viscosity following the ozone bleaching stage.

A subsequent peroxide brightening treatment raises the GE brightness value to at least about 75 for softwoods and about 80 for hardwoods. Preferably, the peroxide treatment is preceded by a metal ion control stage, such as chelation ("Q"), with or without washing. Such control stage treatments are well known in the art and need no further elaboration here.

Thereafter, a medium consistency ozone treatment is conducted to further brighten the pulp. This treatment also activates the pulp to render it more receptive to further brightening with peroxide to the final GE brightness value. The specific brightening sequence of the invention may be carried out along a number of paths as described below, with the option chosen depending primarily upon the type of wood and the final GE brightness which is desired for the finished pulp.

The certain brightness of the delignified pulp is increased by subjecting the pulp to a brightening sequence. In one embodiment, the delignified pulp is treated with a peroxide compound under conditions



sufficient to raise the certain brightness of the pulp to a first increased brightness which is higher than the certain brightness. In another embodiment, the pulp is subsequently treated with ozone under conditions sufficient to raise the first increased brightness of the pulp to a second increased brightness which is higher than the first increased brightness. In a further embodiment, the ozone brightened pulp is treated with a peroxide compound under conditions sufficient to raise the second increased brightness of the pulp to a third increased brightness which is higher than the second increased brightness.

Peroxide treatments are well known in the art and any peroxide stage may be employed herein. These peroxide treatments preferably comprise increasing the pH of the pulp to at least about 9, treating the pulp with a peroxide stabilizing agent and contacting the pulp with a sufficient amount of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the first increased brightness. In the first peroxide treatment step, the pH of the pulp is increased to between about 9.5 and about 11.5, the pulp is treated with a peroxide stabilizing agent and then is contacted with between about 0.2 and 4% by weight based on the oven dry weight of the pulp of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the first increased brightness. The second peroxide treatment is conducted in a similar manner to achieve the third increased brightness, except that lesser amounts of chemical are utilized and the stabilizing agent is generally considered to be optional due to the cleanliness of the pulp at that stage of the process.

The preferred peroxide compound is hydrogen peroxide, and the pH and consistency of the delignified pulp can be adjusted, prior to brightening the pulp, to

ensure a preferred pH of between about 10-11 and a preferred consistency of between about 8-35%. The peroxide stabilizing agent typically would include sodium silicate, magnesium sulfate, EDTA, DTPA or mixtures thereof, and is added to the pulp to prevent  
5 decomposition of the peroxide compound.

The ozone brightening treatment preferably comprises reducing the pH of the peroxide treated pulp to less than about 7 and contacting the pulp at a low or medium consistency of about 1-18% with a sufficient amount of  
10 ozone to achieve the second increased brightness. The pH of the peroxide treated pulp is generally reduced to less than about 4 and the pulp at a preferred consistency of about 5-15% is contacted with a solution containing an  
15 amount of ozone of between about 0.01 and 0.5%, and preferably between about 0.04 and 0.3% by weight based on the oven dry weight of the pulp in a high shear mixing device to achieve the second increased brightness.

The certain brightness is between about 48 and 80 GEB, the first increased brightness is between about 65  
20 and 90 GEB and is increased by at least about 10 to 20 and preferably about 15 to 18 GEB over that of the certain brightness, the second increased brightness is between about 78 and 92 GEB and is increased by at least about 2 to 13 and preferably about 2 to 6 GEB over that  
25 of the first increased brightness, the third increased brightness is between about 83 and 93 GEB and is increased by at least about 1 to 5 and preferably about 1 to 3 GEB over that of the second increased brightness. For softwood, the certain brightness is between about 48  
30 to 70, the first increased brightness is between about 65 to 88, the second increased brightness is between about 78 and 90 and the third increased brightness is between about 83 and 93. For hardwood, the certain brightness is between about 60 to 80, the first increased brightness is  
35 between about 80 to 90, the second increased brightness

is between about 85 and 92 and the third increased brightness is between about 88 and 93. If desired, the pulp may be washed between brightening treatments.

5 A preferred delignification process provides a bleached pulp having a certain brightness and a certain strength as indicated by a certain viscosity which comprises:

chemically digesting a lignocellulosic material to initially form a pulp;

10 oxygen delignifying the pulp to remove a substantial portion of the lignin therefrom, with the combination of the digesting and oxygen delignifying steps being conducted to form an intermediate pulp having a specified amount of lignin and a specified viscosity; and

15 ozone delignifying the intermediate pulp with a gaseous mixture that contains ozone by adjusting the pH of the pulp to below about 4, adjusting the consistency of the pulp to a high consistency of above about 20%, and treating the pulp with an amount of the ozone containing  
20 gaseous mixture sufficient to remove a substantial portion, but not all, of the remaining lignin by intimately contacting and turbulently mixing the pulp particles with the gaseous mixture in a dynamic reaction zone for a sufficient time and at a temperature  
25 sufficient to allow access of the ozone to substantially all of the pulp for reaction therewith while the pulp advances through substantially all of the reaction zone, thus obtaining substantially uniform delignification of a significant portion of the pulp and forming a delignified  
30 pulp having a reduced amount of lignin and the certain strength, viscosity and brightness.

In this process, the specified amount of lignin of the intermediate pulp is such that, after ozone delignification, the delignified pulp attains the certain  
35 GE brightness, and wherein the specified viscosity of the intermediate pulp is sufficiently high to compensate for

viscosity decreases during ozone delignification, thus permitting the delignified pulp to attain the certain strength as evidenced by the certain viscosity.

In addition, the pulp may typically be washed between the various treatment steps with at least a portion of the wash water effluent from one or more of the pulp washing steps being recycled to another pulp washing step. The bleached pulp washing step comprises washing the pulp with fresh water, and separating the pulp from the resulting wash water effluent. Since the bleaching step utilizes a peroxide compound and no materials which preclude its use, at least a portion of the wash water effluent (untreated) can be used to wash the substantially lignin-free pulp.

For countercurrent washing, the substantially lignin-free pulp may be washed with at least a portion of the bleached pulp wash water, with the pulp then being separated from the resulting wash water and at least a portion of the wash water then being used to wash the delignified pulp. The delignified pulp may then be washed with at least a portion of the substantially lignin-free pulp wash water, with the pulp then being separated from the resulting wash water and at least a portion of the wash water being used to wash the intermediate pulp. Next, the intermediate pulp may be washed with at least a portion of the delignified pulp wash water, with the pulp then being separated from the resulting wash water and at least a portion of the wash water being used to wash the initially formed pulp. Finally, the initially formed pulp may be washed with at least a portion of the intermediate pulp wash water, with the pulp then being separated from the resulting wash water so that the wash water can be collected and concentrated prior to incineration in a recovery boiler. In this manner, the water demand for the washing steps is substantially reduced compared to conventional CEDED or

OC/DED processes. The discharge effluent is very low in color and BOD<sub>5</sub> and substantially free of chlorides.

The ozone delignification of the pulp is carried out by dispersing the pulp substantially completely throughout the reaction zone while simultaneously  
5 conveying the pulp through the reaction zone in a plug flow-like manner at a dispersion index of about 7 or less and preferably below about 4.8, thus exposing substantially all of the pulp to the ozone for reaction therewith. This may be accomplished by

10 introducing the high consistency pulp into the reaction zone at a fill level of at least about 10%;

introducing the ozone containing gaseous mixture into the reaction zone for contact with the pulp; and

15 intimately contacting and mixing the pulp with the ozone by lifting, displacing and tossing the pulp in a radial direction to disperse the pulp and expose substantially all of the pulp to the gaseous bleaching agent while advancing the dispersed pulp axially through the reactor in a plug-flow like manner and at the desired  
20 dispersion index for a predetermined time to obtain substantially uniform bleaching of the pulp and to form a bleached pulp having the certain brightness, certain strength and certain viscosity.

Advantageously, the pulp may be fluffed to provide  
25 pulp particles having a first bulk density prior to introduction of the pulp particles into the reaction zone; and the pulp particles may be initially conveying at a first conveying rate followed by conveying the pulp at a second lower conveying rate while simultaneously  
30 increasing the bulk density of the pulp at the first conveying rate to a second increased bulk density at the second conveying rate. If desired, a substantially constant and predetermined fill level of comminuted pulp particles in the reaction zone can be maintained by  
35 initially advancing the relatively low bulk density pulp

particles at the first rate and advancing the increased bulk density particles at a second rate which is less than the first rate. The first conveying rate of the pulp can be gradually reduced to the second conveying rate for enhanced operation.

5 The ozone delignifying step may further comprise removing the gaseous mixture from the reaction zone with entrained pulp particles at a first flow rate; reducing the flow rate of the removed gaseous mixture to a rate where the entrained pulp particles become de-entrained;  
10 and returning the de-entrained pulp particles to the reaction zone. Also, the pulp can be separated from the bleaching gas by removing bleached pulp from the reaction zone; spraying the bleached pulp with water to lower the consistency of the pulp and quench the bleaching  
15 reaction; and directing the pulp into receiving means by angling the water spray towards the receiving means.

An advantageous ozone delignifying step comprises: increasing the consistency of the intermediate pulp to at least about 28%;

20 comminuting the increased consistency pulp into discrete particles of a predetermined particle size having a sufficiently small diameter and a sufficiently low density to facilitate substantially complete penetration of a majority of the pulp particles by ozone  
25 gas without causing significant degradation of the cellulose components of the pulp; and

uniformly contacting the comminuted pulp particles and the ozone containing gaseous mixture during the turbulent mixing step while the pulp is advanced through  
30 the reaction zone for a sufficient time to obtain substantially uniform delignification of a majority of the pulp particles.

The comminuted pulp particles may be advanced through the reaction zone countercurrently to the ozone  
35 containing gaseous mixture for contacting the pulp

particles which have been bleached to the greatest extent with the ozone containing gaseous mixture containing the maximum concentration of ozone and for contacting the pulp entering the reaction zone with the ozone containing gaseous mixture containing a nearly exhausted ozone concentration, thereby providing optimum consumption of the ozone and uniform delignification of substantially all of the pulp particles. In this regard, the pulp particles may be contacted and mixed with the gaseous bleaching agent by operating conveying means having a plurality of paddle blades arranged upon a rotatable shaft.

The process may be further optimized by controlling at least one of the fill level or residence time of the pulp particles in the reaction zone by selecting a particular paddle design, spacing, pitch, shape or surface area in combination with the rotational speed of the shaft, or by modifying at least one of the paddle design, spacing, pitch, shape or surface area to reduce conveying efficiency and rotating the shaft at higher RPM to compensate for such reduced conveying efficiency, thus obtaining one or more of (1) efficient contact of the pulp particles with the gaseous mixture, (2) increased conversion of the ozone or (3) a substantially constant fill level of pulp particles in the reaction zone.

The oxygen delignification step may be conducted by forming a low to medium consistency pulp; treating the low to medium consistency pulp with an aqueous solution of an alkaline material for a predetermined time and at a predetermined temperature relative to the quantity of the alkaline material to substantially uniformly distribute the alkaline material throughout the low to medium consistency pulp; raising the consistency of the pulp to a high consistency; and subjecting the resulting high consistency pulp to high consistency oxygen delignification to obtain the intermediate pulp.

Alternatively, the oxygen delignification treatment may be carried out conventionally on medium consistency pulp.

The oxygen delignification step can be conducted by applying a first amount of alkaline material to brownstock pulp having a consistency of about 10% by weight or less and preferably a low consistency of about 5% or less by combining the pulp with a sufficient quantity of alkaline material with uninterrupted mixing in a manner to ensure that all pulp fibers are exposed to the alkaline material to obtain a substantially uniform distribution of alkaline material throughout the pulp and then increasing the consistency of the alkaline material containing pulp to at least about 18% by weight to obtain high consistency pulp and to remove liquid while retaining the first amount of alkaline material substantially uniformly distributed throughout the high consistency pulp, with the pulp fibers containing the alkaline material being directly passed from the combining step to the consistency increasing step;

optionally applying a second amount of alkaline material onto the high consistency pulp to obtain a total amount of alkaline material on the pulp of at least about 0.8 to 7 percent by weight based on the oven dry weight of the pulp, wherein at least about 55% to 100% of the total amount of alkaline material is applied to the pulp during the alkaline material combining step; and

subjecting the increased consistency alkaline material containing pulp to high consistency oxygen delignification to obtain enhanced delignification of the pulp without a corresponding decrease in pulp viscosity compared to pulp which is not combined with alkaline material at low consistencies and form an intermediate pulp having a specified amount of lignin and having a specified viscosity.

The consistency of the pulp which is combined with the aqueous alkaline solution prior to oxygen



delignification preferably ranges between about 1 and 4.5% by weight, the consistency of the pulp is increased to between at least about 25% by weight prior to the oxygen delignification step, the high consistency pulp contains an amount of alkaline material of between about 0.8 to 7 percent by weight based on the oven dry weight of the pulp prior to oxygen delignification, and preferably, at least a significant portion of the liquid removed from the consistency increasing step is directly recycled to the alkaline material combining step. Also, the pulp is typically directed to oxygen delignification without any intervening delignification or bleaching steps, and at least about 60% of the liquid removed from the consistency increasing step is directly recycled to the alkaline material combining step.

If desired, prior to the alkaline material combining step, the pulp can be provided with a consistency which is equal to or greater than that of the high consistency pulp which is to be formed so that substantially all removed liquid can be directly recycled to the alkaline material combining step. A predetermined quantity of removed liquid may be accumulated in order to continuously recycle such liquid directly to the alkaline material combining step in the event of intermittent or non-continuous operation of the consistency increasing step. Also, a portion of the liquid removed from the pulp can be recycled for washing the pulp prior to applying the alkaline material.

When the pulp is unbleached softwood pulp, the amount of alkaline material applied to the pulp is between about 1.5 and 4 percent by weight, while for unbleached hardwood pulp, the amount of alkaline material applied to the pulp is between about 1 and 3.8 percent by weight. Thus, after oxygen delignification, the intermediate pulp has a K No. of about 14 or less and a viscosity of greater than about 10 cps, while after ozone

delignification, the delignified pulp has a K No. of about 6 or less, a viscosity of greater than about 7 cps and a brightness of at least about 35 GEB. Preferable values for softwood include, after the oxygen step, a K No. of about 11 or less and a viscosity of greater than about 12 cps, while after the ozone step, a K No. of about 5 or less, a viscosity of greater than about 9 cps, and a brightness of at least about 45 GEB. Preferable values for hardwood include, after the oxygen step, a K No. of preferably about 9 or less and a viscosity of greater than about 12 cps, while after the ozone step, a K No. of about 5 or less, a viscosity of greater than about 9 cps, and a brightness of at least about 55 GEB.

In this embodiment, the intermediate pulp can be delignified with an effective amount of ozone for a sufficient time to obtain a delignified pulp having a reduced amount of lignin and the certain GE brightness, strength and viscosity. Typically, the intermediate pulp is directed to ozone delignification without any intervening delignification or bleaching steps.

The lignocellulosic material may be chemically digested by Kraft pulping, Kraft AQ pulping or extended delignification to form the pulp. A chelating agent, such as DTPA, EDTA or oxalic acid, may be added to the intermediate pulp prior to ozone delignification to render metal ions therein substantially non-reactive to ozone and increasing the consistency of the pulp to at least about 20% by weight prior to ozone delignification.

#### Brief Description of the Drawings

Fig. 1 schematically illustrates the pulping, oxygen delignification and ozone delignification steps which comprise the bulk delignification portion of the process of the invention;

Figs. 2 and 3 schematically illustrate the various brightening sequences which may be used in the process of

the present invention to produce a final pulp having the desired brightness;

Fig. 4 is a graph of GE brightness for several ozone application levels on softwood pulp (a Kraft AQ  $O_m$   $Z_m$  E pine) which was further treated by either a  $R(QP)Z_2$  or  $RZ_2$  sequence;

Fig. 5 is a graph of brightness versus applied peroxide in the second peroxide stage for pulps which were treated with several intermediate stages;

Fig. 6 is a graph of viscosity verses GE brightness for the intermediate treatments of Fig. 5;

Figs. 7 and 8 are graphs comparing the GE brightness attained verses % ozone consumed for various brightening sequences; and

Figs. 9-12 are results of GE brightness and viscosity versus applied amounts of reduction agent and applied ozone for pulps treated with such chemicals.

#### Detailed Description of the Preferred Embodiments

##### A. Pulping

The first stage in the method of the present invention is the pulping step. Here, procedures may be utilized which improve the amount of lignin removed from the lignocellulosic material, while minimizing the amount of degradation of the cellulose.

A processing scheme for carrying out the "front end" of the method of the present invention is illustrated in schematic form in Fig. 1. Wood chips 2 are introduced into a digester 4 together with a white liquor 6 comprising sodium hydroxide, sodium sulfide and, in the preferred embodiment, an anthraquinone additive. Sufficient white liquor should be introduced into digester 4 to substantially cover the wood chips. The contents of digester 4 are then heated at a temperature and for a time sufficient to allow the liquor to substantially impregnate the wood chips.

The use of the Kraft/AQ pulping technique is preferred since the inclusion of the anthraquinone additive contributes significantly to the degree of lignin removal without causing significant adverse affects upon the desired strength characteristics of the remaining cellulose. The amount of anthraquinone in the cooking liquor should be at least about 0.01% by weight, based upon the oven dried ("OD") weight of the wood to be pulped, with amounts of from about 0.02 to 0.1% generally being preferred. Although the Kraft/AQ technique costs more to perform than, for example, an unmodified Kraft treatment, this additional cost is at least partially offset by the savings in the cost of chemicals needed for the subsequent oxygen, ozone and brightening stages and the increased yield in the resulting pulps.

Alternately, or perhaps even in addition to the use of the Kraft/AQ process, the pulping stage can be carried out with the use of techniques for extended delignification such as the Kamyr MCC and EMCC or isothermal cooking, Beloit RDH and Sunds Cold Blow methods. These techniques also offer the ability to remove more of the lignin during cooking without adversely affecting the desired strength characteristics of the remaining cellulose to a significant degree.

Still further, the pulping stage may be carried out, if desired, with the use of an unmodified Kraft process. The Kraft process is not particularly practical for use in the present invention unless it is coupled with an oxygen treatment which is sufficient to remove correspondingly more lignin in the oxygen delignification step without adversely affecting the strength of the oxygen delignified pulp. This combination is capable of producing a pulp of sufficient brightness and viscosity to permit effective ozone and peroxide bleaching to the high GEB values stated above. In contrast, the combination of Kraft pulping plus "standard" oxygen

delignification (described below) produces a pulp which does not retain sufficient viscosity, i.e., strength, to form a useful product after completion of the remaining delignification and bleaching steps.

5 The pulping step is conducted so that, for a southern U.S. softwood, for example, conventional Kraft pulp with a K No. in the range of about 20-24 (target of 21), a CED viscosity in the range of about 21-28, and a GE brightness in the range of about 15-25 is typically obtained. For southern U.S. hardwood, conventional Kraft  
10 pulp with a K No. in the range of about 10-14 (target 12.5) and a CED viscosity of about 21-28 is typically obtained.

Turning again to Fig. 1, the digester 4 produces a black liquor containing the reaction products of lignin  
15 solubilization together with the brownstock pulp 8. The cooking step is typically followed by washing to remove most of the dissolved organics and cooking chemicals for recycle and recovery, as well as a screening stage (not shown) in which the pulp is passed through a screening  
20 apparatus to remove bundles of fibers that have not been separated in pulping. The brownstock 8 is treated in washing units comprising, in sequence, a blow tank 10 and washing unit 12 where residual liquor 14 contained in the  
25 pulp is removed.

#### B. Oxygen Delignification

The next stage in the process of the present invention, i.e., the oxygen delignification step, primarily involves removal of residual lignin from the  
30 brownstock pulp. In accordance with conventional high consistency oxygen delignification techniques (i.e., "O"), the washed pulp is pressed to a high consistency of at least about 25% and an aqueous alkaline solution is then sprayed onto the resultant fiber mat to deposit from  
35 about 0.8 - 7% by weight of the alkaline material onto

the pulp. The high consistency alkaline fiber mat is then subjected to oxygen delignification to remove a substantial portion of the lignin from the pulp. When used to obtain substantial decreases in K No., i.e., greater than 50%, this procedure is known to cause substantial decreases in pulp viscosity, i.e., strength. Thus, it is important to couple this technique with one of the more efficient pulping processes, such as Kraft/AQ and/or extended delignification, in order to obtain pulp with sufficiently low K Nos. for use in the remainder of the present bleaching process.

It has been found that the oxygen delignification treatment may be modified and conducted in a manner which allows for the removal of increased percentages of the lignin remaining in the brownstock pulp without causing an unacceptable corresponding decrease in the viscosity of the pulp. This allows conventional Kraft pulping to be used with such modified oxygen delignification techniques while still obtaining the desired K Nos. and viscosities.

In one process, designated herein as O<sub>m</sub> (m=modified), the brownstock pulp is treated at low to medium consistency with an amount of alkali necessary to ensure uniform application thereof upon the pulp. The brownstock is maintained at a pulp consistency of less than about 10% and preferably less than about 5% by weight. The consistency of the pulp is generally greater than about 0.5%, however, since lesser consistencies are not economical to process in this manner. A most preferred consistency range is 0.5 to 4.5%. Thereafter the consistency of the pulp is raised to at least 18 percent. Preferably the pulp consistency is raised from about 20-25% to about 35%, and even more preferably, to about 27%. Thereafter the high consistency pulp is directed to an oxygen reactor for delignification using conventional conditions.

The advantage of using the  $O_m$  process is illustrated by comparison of the K Nos. and viscosities obtained using southern softwoods to those obtained with the  $O$  process under otherwise substantially identical process conditions. Using a conventional Kraft pulping procedure and conventional high consistency oxygen delignification bleaching, the pulp thus obtained will typically have a K No. of about 12 to 14 and a viscosity of about 15. This K No. is too large to permit later delignification using the ozone stage of the present invention. However, the use of conventional Kraft pulping with the modified high consistency oxygen bleaching surprisingly results in a pulp having a K No. of less than about 9, while the viscosity of the pulp is maintained above about 12 to 14.

These two values, i.e., K No. and viscosity, are related in that the ratio of the change in viscosity to the change in K No., referred to as the "delignification selectivity" of the process, is a measure of the efficiency of the  $O_m$  technique for removing lignin while maintaining adequate levels of viscosity therein. The use of the  $O_m$  process, as described above, thus results in an enhanced degree in the selectivity of the delignification, signified by a reduction in K No. of at least about 20% greater than that obtained with the use of an "O" stage. Thus, the combination of Kraft pulping and  $O_m$  oxygen delignification will result in an enhanced delignification selectivity, i.e., a sufficiently low K No. and a sufficiently high viscosity, to permit further delignification and bleaching by ozone and peroxide.

Further details of the  $O_m$  oxygen delignification process are disclosed in U.S. Patent 5,217,574, the disclosure of which is expressly incorporated herein by reference thereto.

Alternately the oxygen delignification treatment may be carried out using a two-stage "O," (s = split) alkali addition. In this stage a first amount of alkaline

material is applied to pulp at low consistency by combining the pulp with a quantity of alkaline material in an aqueous alkaline solution. The consistency of the pulp is then increased to a high consistency of at least about 18%. Next, a second amount of alkaline material is  
5 applied to the high consistency pulp to obtain a total amount of alkaline material applied to the pulp. After this treatment, the pulp is then subjected to oxygen delignification whereby the enhanced delignification selectivities of the  $O_m$  process are achieved.

10 While the  $O_m$  process is preferred over the standard "O" method, the alternate  $O_t$  technique is most preferred because a lower proportion of the alkaline material (i.e., than with the  $O_m$  process) is applied to the low consistency pulp. This, in turn, reduces the amount of  
15 alkaline material utilized in mixing chest 18 and also reduces the amount of this material removed via pressate discharge 32 (see below). Thus, splitting the application of the alkaline material between the high and low consistency pulp reduces the amount of pressate  
20 discharge 32 which, in turn, reduces the amount of alkaline material which must be reintroduced, thus saving chemical. Further the high consistency alkaline treatment portion of the  $O_t$  method permits rapid  
25 modification of the amount of the alkaline material present in the pulp entering the oxygen delignification reactor to compensate for changes in the properties (i.e., wood type, Kappa or K. No. and viscosity) of the incoming brownstock, or to vary the degree or extent of oxygen delignification for a particular pulp.

30 Referring again to Fig. 1, washed brownstock 16 is introduced into a mixing chest 18 where it is substantially uniformly treated with sufficient alkaline material 20 for a time sufficient to distribute a first amount of alkaline material throughout the pulp. The low  
35 consistency treatment portion of this  $O_t$  process is



carried out in the same manner as the  $O_m$  process, but less alkaline material (i.e., about half as much) is applied to the pulp. In the  $O_m$  process, an aqueous sodium hydroxide solution is combined with the low consistency pulp in an amount sufficient to provide  
5 essentially the same amounts on the OD pulp as was achieved by the  $O$  process. In the  $O$  process, at least about 0.4% to about 3.5% by weight of sodium hydroxide is deposited on the pulp, based on oven dry ("OD") pulp after thickening with the balance applied to the high  
10 consistency pulp. Other alkali sources having equivalent sodium hydroxide content can also be employed instead of sodium hydroxide if desired. Oxidized white liquor is a convenient plant stream which may be utilized.

The alkaline treated pulp 22 is forwarded to a  
15 thickening unit 24 such as a twin roll press where the consistency of the pulp is increased to the desired value. The pulp consistency increasing step also removes residual liquid or pressate 26. A portion 28 of this pressate 26, may be directly recycled back to brownstock  
20 washer 12. Alternately, a portion 30 may instead be directed to mixing chest 18 for use in the low consistency pulp alkaline treatment step. Since the consistency of the pulp is increased in the thickening unit 24, a certain amount 32 of pressate may continually  
25 be discharged to the plant liquid recovery system to maintain water balance in the mixing chest 18.

Additional alkaline material 36 is applied to the high consistency brownstock 34 produced by the thickening unit 24 to obtain the desired total amount of alkaline  
30 material on the pulp prior to oxygen delignification. This total amount of alkaline material is selected to achieve the desired extent of delignification in the subsequent oxygen delignification step which is carried out on the alkaline material treated high consistency  
35 pulp. The total amount of alkaline material actually

applied onto the pulp will generally be between 0.8 and 7% by weight based on oven dry pulp, and preferably between about 1.5 and 4% for southern softwood and between about 1 and 3.8% for hardwood. About half these amounts are preferably applied in each of the low  
5 consistency and high consistency treatments. Thus, about 0.4 to 3.5% by weight, preferably about 0.5 to 1.9% for hardwood and 0.75 to 2% for softwood, is applied onto the pulp during each of the low and high consistency alkaline treatments.

10 Further details concerning the "O<sub>2</sub>" process are set forth in U.S. Patent 5,173,153, the disclosure of which is expressly incorporated herein by reference thereto.

The alkaline treated pulp 38 is then forwarded to the oxygen delignification reactor 40 where it is  
15 contacted with gaseous oxygen 42. Suitable conditions for oxygen delignification according to either the O<sub>2</sub>, O<sub>2</sub>, or O<sub>2</sub> processes comprise introducing gaseous oxygen at about 80 to about 100 psig to the high consistency pulp while maintaining the temperature of the pulp between  
20 about 90 and 130°C. The average contact time between the high consistency pulp and the gaseous oxygen ranges from about 15 minutes to about 60 minutes.

After oxygen delignification in reactor 40, the partially delignified pulp 44 is forwarded to washing  
25 unit 46 wherein the pulp is washed with water 48 to remove any dissolved organics and to produce high quality, low color pulp 50. A first portion 54 of the oxygen stage washer 46 filtrate 52 can be used to advantage in a first shower on the brownstock washer 12.  
30 This improves washing and reduces the pressate portion 55 which is used in a second shower on washing unit 12 and later returns into the residual liquor 14 which is sent to the plant recovery without further reuse. A second  
35 portion 56 of filtrate 52 is discharged directly to the plant recovery system.

Upon completing the oxygen delignification stage, the delignification selectivity of the pulp is enhanced in that the K No. of the pulp is decreased by at least about 50%, compared to the decrease of no more than about 50% with conventional oxygen delignification systems, without significantly damaging the cellulose component of the pulp. The GEB brightness of the pulp after this stage is generally between about 35 and 50 depending upon the type of pulp and the specific pulping conditions utilized. For the softwood pulp described above, a K No. of about 7-10 and a viscosity of above about 13 is readily achieved. For hardwood pulp, a K No. of about 5-8 and a viscosity above about 13 is obtained after the oxygen delignification step.

15 c. Ozone Delignification/Bleaching

The next step in the process of the invention is ozone delignification and bleaching of the oxygen-delignified brownstock pulp. Treating pulp at high consistencies with ozone without paying particular attention to the comminution of the pulp fibers or to the contact between the individual fibers and the reactant gas stream invariably results in a non-uniform ozone bleaching of the fibers. Such a non-uniform ozone treatment is designated in the prior art with the letter "Z". While the use of a Z stage is not desirable due to the non-uniformities produced, there are situations where the resulting pulp is useful. However, it is preferred to use a modified ozone technique in which the fibers in a desired size range are uniformly contacted with the ozone gas stream. This ozone treatment has been designated herein as "Z<sub>m</sub>".

Prior to treatment with ozone, the pulp is conditioned so as to ensure the most effective selective delignification and to minimize the chemical attack of the ozone on the cellulose. As illustrated in Fig. 1,

the incoming pulp 50 is directed into a mixing chest 58, where it is diluted to a low consistency. An organic or inorganic acid 60 such as sulfuric acid, formic acid, acetic acid or the like, is added to the low consistency pulp to decrease the pH of the pulp in mixing chest 58 to the range of about 1 to 4 and preferably between 2 and 3.

The acidified pulp is treated with chelating agent 62 to complex any metals or metal salts which may be present therein. This chelating step is used to render such metals non-reactive or harmless in the ozone reactor so that they will not cause breakdown of the ozone, thus decreasing the efficiency of the lignin removal and also reducing the viscosity of the cellulose. Preferred chelating agents for this ozone treatment, for reasons of cost and efficiency, include diethylenetriamine pentacetic acid ("DTPA"), ethylenediamine tetraacetic acid ("EDTA") and oxalic acid. Amounts of these chelating agents ranging from about 0.1% to about 0.2% by weight of OD pulp are generally effective, although additional amounts may be needed when high metal ion concentrations are present.

The acidified, chelated, low-consistency pulp 64 is introduced into a thickening unit 66, such as a twin roll press, for removing excess liquid 68 from the pulp, wherein the consistency of the pulp is raised to a level above about 20%. At least a portion of this excess liquid 68 may be recycled to mixing chest 58 with a remaining portion 68a being directed to the plant recovery. The resultant high consistency pulp 70 is then passed through compaction device 72 such as a screw feeder which acts as a gas seal for the ozone gas and thereafter through a comminuting unit 74, such as a fluffer, for use in reducing the pulp particle size as described below.

A preferred range of consistency, especially for southern U.S. softwood, has been found to be between

about 28% and 50%, with the optimum results being obtained at between about 38% and 45% prior to contact with ozone. Within the above ranges, preferred results are obtained as indicated by the relative amount of delignification, the relatively low amount of degradation of the cellulose, and the noticeable increase in the brightness of the treated pulps.

The reaction temperature at which the ozone bleaching is conducted is likewise an important factor in the process of the present invention. The maximum temperature of the pulp at which the reaction should be conducted should not exceed the temperature at which excessive degradation of the cellulose occurs, which with southern U.S. softwood is a maximum of about 120°F to 150°F.

An important feature of the ozone stage of the invention is that the pulp be uniformly bleached by the ozone. This uniform bleaching is obtained, in part, by comminution of the pulp into discrete floc particles of a size which is of a sufficiently small diameter and of a sufficiently low bulk density so that the ozone gas mixture will completely penetrate a majority of the fiber flocs. Generally, a comminuted pulp particle size of 10mm or less has been found to be acceptable.

During the ozone bleaching process, the particles to be bleached should be exposed to the gaseous ozone bleaching agent by mixing so as to allow access of the ozone gas mixture to all surfaces of the flocs and equal access by the ozone gas mixture to all flocs. The mixing of the pulp in the ozone gas mixture gives superior results with regard to uniformity as compared to the results obtained with a static bed of flocs which results in channeling wherein some of the flocs are isolated from the ozone gas relative to other flocs and are thereby bleached less than other flocs.

Upon exiting fluffer 74, the oxygen delignified pulp particles 76 enter a reactor apparatus 78 adapted for bleaching these particles from a first GE brightness to a second, higher GE brightness. The pulp fiber particles 76 are bleached by the ozone in reactor 78 typically to  
5 remove a substantial portion, but not all, of the lignin therefrom. A preferred apparatus comprises a paddle reactor as described in U.S. Patent 5,181,989 and U.S. patent application serial no. 07/821,117, the disclosure of each of which is expressly incorporated herein by  
10 reference thereto.

As the pulp particles are advanced through this reactor, an internal conveyor 80, preferably in the form of a rotating shaft 82 to which is attached a plurality of paddle members 84, powered by motor 86, is used to  
15 provide intimate contact and mixing between the pulp particles and the ozone gas. These conveying means displace and toss the pulp particles in a radial and forward direction while also inducing the ozone to flow and surround the displaced and tossed pulp particles, to  
20 expose substantially all surfaces of a majority of these particles to the ozone. This facilitates substantially complete penetration of all surfaces of these particles by the ozone.

At low RPMs, the paddles move the pulp in a manner  
25 such that it appears to be "rolling" or "lifted and dropped" through the reactor. At higher RPMs, the pulp is dispersed into the gas phase in the reactor, with the pulp particles uniformly separated and distributed throughout the gas, causing uniform bleaching of the  
30 pulp. The overall bleaching rate of the pulp particles is thus significantly improved compared to prior art bleaching methods utilizing fast-reacting gaseous bleaching agents such as ozone.

The forward movement of the dispersed pulp  
35 approximates plug flow and facilitates a high degree of

bleaching uniformity. The reactor is operated at a dispersion index of less than 7, preferably less than about 4.8, at all rotational speeds of less than about 125 rpm and is designed to simultaneously control pulp contacting, pulp residence time and gas residence time while effectively consuming up to 99 percent of the ozone. In this way the pulp is bleached to the desired degree while a significantly high conversion of ozone gas bleaching agent is achieved.

The ozone gas which is used in the bleaching process may be employed as a mixture of ozone with oxygen and/or an inert gas, or it can be employed as a mixture of ozone with air. The amount of ozone which can satisfactorily be incorporated into the treatment gases is limited by the stability of the ozone in the gas mixture.

Conventional ozone gas mixtures which now typically contain about 1-14% by weight of ozone in an ozone/oxygen mixture, or about 1-7% ozone in an ozone/air mixture, are suitable for use in this invention. The ozone gas can be introduced at any position through the outer wall of the shell of the reactor.

As shown in FIG. 1, ozone gas 88 is introduced into the reactor 78 in a manner such that it flows, in one embodiment of the invention, countercurrent to the flow of the pulp.

Any residual ozone gas 90, as it exits reactor 78, is directed to a carrier gas pretreatment stage 92 where a carrier gas 94 of oxygen or air is added. This mixture 96 is directed to ozone generator 98 where the appropriate amount of ozone is generated to obtain the desired concentration. The proper ozone/air or ozone/oxygen mixture 100 is then directed to reactor vessel 78 for delignification and bleaching of pulp particles 76. A further description and discussion of the reaction conditions utilized in the ozone delignification stage of the invention can be found in

U.S. Patent 5,164,043, the disclosure of which is expressly incorporated herein by reference thereto.

Pulp fiber flocs 102, after treatment, are directed into tank 104 by spray from water nozzles which create a water shower that soaks the pulp and quenches the ozone  
5 bleaching reaction on the pulp particles. It is desirable that the quenching occur as uniformly and as quickly as possible in order to preserve the bleaching uniformity achieved in the reactor apparatus. Thus, these nozzles are arranged to provide an even, soaking  
10 shower of water while also being angled downward at an angle of at least 30° with respect to the horizontal and preferably at about 45°, in order to force the pulp down into the tank and avoid the formation of a water curtain which would inhibit the free fall of the pulp. The pulp  
15 collected in tank 104 has a consistency of about 6% and is washed and recovered or transported to subsequent brightening treatments.

Pulp exiting the ozone reactor has a GE brightness of at least about 48 percent and generally around 50 to  
20 80 percent, with hardwoods usually being above about 60 percent. The pulp (for hardwoods or softwoods) also has a K No. of between about 3 and 6.

For certain papermaking processes, a final pulp brightness in the upper end of this range is  
25 satisfactory. When it is necessary to further raise the pulp brightness to higher GEB values, the substantially delignified pulp from the  $Z_m$  stage is subsequently subjected to the brightening sequence, which is primarily intended to remove most or all of the remaining lignin  
30 and convert any remaining chromophoric groups on the lignin in the pulp into colorless derivatives. Often, the pulp 102 exiting the ozone reactor is already of sufficient minimum initial GE brightness (i.e., at least about 59) for certain uses so that further brightening is  
35 not necessary.



#### D. Optional Extraction Sequences

When further brightening is desired, an extraction stage (i.e., E) prior to such further brightening may be conducted. If an extraction stage is used or desired, it may be conducted as described in the aforementioned '043 patent, i.e., by mixing the pulp with an alkaline material to solubilize a substantial portion of the lignin which remains in the pulp. The E stage can be augmented with either oxygen, peroxide or oxygen and peroxide, if desired.

The use of oxygen or hydrogen peroxide enhances the reduction of kappa number (or K No.) during the extraction stage. It is also possible and advantageous to include an additive to prevent loss of viscosity during such extractive treatments. One well known additive for this purpose is sodium borohydride. Further information about these additives can be found in an article by Lindholm, "Alkaline Extraction of Ozone-Bleached Pulp," Journal of Pulp and Paper Science, Vol. 19, No. 3, May, 1993, which summarizes the effects and benefits of such additives in various extraction processes. In addition, additives such as formamidine sulfinic acid or sodium hydrosulfite can instead be used for the same purposes. When such additives are used, the extraction is referred to as a reduction stage ("R").

One advantageous way to conduct extractions is to add an alkaline material such as sodium hydroxide to the water in tank 104. As with any extraction stage, the addition of alkaline material decreases the amount of oxidant required in the subsequent bleaching sequence, and the cost of alkaline material is less than the cost of the subsequently used brightening agents. The alkaline material is added in an amount sufficient to raise the pH of the pulp to between about 7 to 8, since these higher values are necessary when a peroxide compound is used for further brightening of the pulp.

E. Preferred Brightening Sequences

1. The First Peroxide Stage

After completion of the ozone bleaching step, or after the completion of the extraction step, the substantially delignified pulp 102 is again thoroughly washed in washer 106 as shown in Fig. 2. The washed pulp has a pH near neutral and a consistency of about 16%. Since chlorine containing compounds have not been used to delignify the pulp, it is possible and often desirable to recycle at least a portion of the effluent 108 which is recovered from washing unit 106 to washing unit 46, as this produces environmental benefits due to the elimination of what would otherwise be sewer liquid.

At this stage of the process, several different brightening treatments may be selected with the particular one chosen depending on the type of wood pulp, the brightness of the pulp after the ozone stage and the desired GEB desired for the final product. The consistency and pH of the pulp 110 exiting the washer 106 must therefore be adjusted prior to carrying out the desired brightening treatments.

When the first brightening stage uses a peroxide compound, the pulp is first conditioned in a tank 112, where a chelant (such as EDTA or DTPA) 116 is added with water to sequester undesirable metal ions which could cause decomposition of the peroxide brightening agent. The consistency of the pulp is reduced to about 3-12% and the pH remains at about 7 to 8 while the pulp is held at about 90°C for about 1 hour. The need for this treatment is dependent on the metal ion type, its amount in the pulp 110 and its accompanying dissolved solids.

The pulp 120 which exits tank 112 is thoroughly washed in a washer 124 to remove the chelants and any sequestered metal ions. The washed pulp 128 again has a pH near neutral and a consistency of about 16%. The wash

35

water 122 for this washer 124 would generally be fresh water.

The washed pulp 128 then is directed into a peroxide brightening tower 130, where a solution 132 of alkaline material and a peroxide compound, such as hydrogen peroxide, is added. This adjusts the consistency of the pulp to a range of between about 8-35%, while the pH of the pulp is adjusted upwardly to ensure a final pH of about 9.5 to 11. A peroxide stabilizing agent 134, selected from sodium silicate, magnesium sulfate, a chelant (such as EDTA or DTPA) or mixtures thereof, can be added in an amount sufficient to prevent the undesirable decomposition of the hydrogen peroxide bleaching agent. The stabilizing agents are added on a weight percent basis based upon the weight of the pulp, with preferred ranges of use being up to 3% of sodium silicate, up to 0.2% magnesium sulfate, i.e., as magnesium ( $Mg^{++}$ ) and up to 0.2% of the chelate. When the effluent from washing the peroxide brightened pulp is to be recycled, the preferred stabilizing agent is magnesium sulfate.

The solution 130 to be added will generally include between about 0.25 and 4% by weight of a peroxide solution, preferably hydrogen peroxide, based upon the weight of the pulp. When hardwoods or other relatively easy to bleach woods are utilized, the peroxide treatment can be conducted by contacting the pulp with lesser amounts of the chemical within this range, while softwoods would require greater amounts of chemical which would typically be about 0.75 to 1%. The reaction is conducted in a brightening tower 130 for sufficient time to increase the brightness of the pulp to the desired levels. Generally, a GE brightness of about 67 to 88 and preferably above about 75-80 GEB is attained. The brightness value achieved will depend upon the amounts of

chemical used and the brightness of the pulp as it enters into the peroxide brightening stage.

The specific peroxide compound to be used, which is generally hydrogen peroxide, as well as the particular stabilizer combinations are considered to be conventional and well within the knowledge of one skilled in the art.

The pulp 140 which exits tower 130 is again thoroughly washed in a washer 144 using recycle water 168 or fresh water 142. The washed pulp 148 again has a pH near neutral and a consistency of about 16%. The wash water effluent 146 from this washer 144 can be used to advantage as the washing water for washer 106, since no chlorine containing chemicals were used in the previous brightening stage.

## 2. Medium Consistency Ozone Brightening

Where higher brightness values are desired for the final pulp, an ozone stage may be conducted after the first peroxide treatment. Unlike the initial ozone stage, which conducts bulk delignification on high consistency pulp using a specially designed reactor for turbulently mixing the pulp and the ozone gas bleaching agent in order to obtain uniform bleaching, the second ozone stage utilizes a much lower amount of ozone chemical with a high shear mixing device to achieve substantial brightness increases and to activate the pulp previously treated with peroxide to achieve enhanced response in a second peroxide stage, if one is employed. This second ozone stage applies a relatively small amount of between about 0.01 and 0.5% by weight ozone based on the weight of OD pulp to obtain a relatively large increase in brightness to between about 78 and 90 GEB, and preferably above about 85 GEB.

Since any commercial plant designed to conduct the delignification and bleaching steps of the present invention would include the particular ozone reactor for

conducting the bulk delignification, the plant would already include a source or supply of ozone and the appropriate chemical treatment lines for conditioning the pulp prior to reaction with ozone. Thus, appropriate piping could be connected to these supplies to provide  
5 the necessary ozone, acid and chelating chemicals for treatment of the pulp in this stage.

As shown in Fig. 3, pulp 148 exiting the first peroxide treatment would be directed into a chest or  
10 mixing tank 150 where the pulp can be combined with the appropriate chelation agents and acids to form an acidic chelated low to medium consistency pulp 158. The particular consistency of the pulp can be between about 1 and 15% with between about 1-5% used for low consistency and between about 6 and 15% used for medium consistency,  
15 with one of ordinary skill in the art being capable of selecting the particular consistency for the desired final pulp. An ozone gas mixed with water 156 is also added to the tank 150. The concentration of the ozone gas in the high shear mixer 160 is adjusted so that an  
20 application of about 0.01 to 0.5%, and preferably between about 0.04 and 0.3% by weight based on the O.D. weight of the pulp is applied.

The acidic chelated low to medium consistency pulp 158 is then directed into a high shear MC mixer 160 as  
25 disclosed in U.S. Patent 5,145,557, the content of which is expressly incorporated herein by reference thereto. Thus, the ozone and pulp are substantially uniformly combined so that the ozone has access to all pulp particles for reaction therewith. Since the ozone-pulp  
30 reaction is very rapid, the pulp contact with ozone gas in the mixer is sufficient to brighten the pulp to the desired values. As noted above, a typical GEB after this stage would be about 85 or greater.

After the pulp is treated with ozone in the high  
35 shear mixer 160, the pulp 161 is directed to a residence

tower 162 where the ozone-pulp reaction can continue. Spent gas exits the tower 162 at line 165 and can be recycled with the other spent gas from reactor 78 to the carrier gas pretreatment stage 92. The ozone treated pulp 163 is thoroughly washed in a washer 164. It has  
5 also been found that the ozone brightening step activates the pulp, thus making it more receptive to bleaching by a subsequent peroxide stage. A solution of alkaline material is used as the wash water 166 so that the washed pulp 170 will have a pH near neutral and a consistency of  
10 about 16%. The wash water effluent 168 can be recycled as for washing the pulp after any of the previous delignification stages.

### 3. Further Peroxide Brightening

15 For certain woods, such as the difficult to bleach softwoods, it may be necessary to conduct a further brightening stage to achieve the final desired brightness of the pulp. Thus, a second or final peroxide stage  
20 could be conducted using in the same manner as described above, except that significantly lower amounts of peroxide chemical can be used. It is anticipated that this stage would be conducted utilizing approximately  
25 one-half the amount of chemical that is used in the first peroxide stage, i.e., about 0.1 to 1, preferably about 0.1 to 0.6 and most preferably about 0.3 to 0.4 %.

The washed pulp 170 is directed into a peroxide brightening tower 172, where a solution 174 of alkaline material and a peroxide compound, such as hydrogen  
30 peroxide, is added. This adjusts the consistency of the pulp to a range of between about 10-15%, while the pH of the pulp is adjusted upwardly to ensure a final pH of about 9.5-11. A peroxide stabilizing agent 176, selected  
35 from sodium silicate, magnesium sulfate, a chelant (such as EDTA or DTPA) or mixtures thereof, can be added in an amount sufficient to prevent the undesirable

decomposition of the hydrogen peroxide bleaching agent. The preferred stabilizing agent is magnesium sulfate. The stabilizing agents are added on a weight percent basis based upon the weight of the pulp. Lesser amounts of these agents are used compared to the first peroxide stage, with preferred ranges of use being up to 1.5% of sodium silicate, up to 0.1% magnesium sulfate, i.e., as magnesium ( $Mg^{++}$ ) and up to 0.1% of the chelant. Also, use of these additives may not be necessary since the condition of the pulp is relatively clean at this point in the process.

The solution 174 to be added will generally include between about 0.1 and 1% by weight of a peroxide solution, preferably hydrogen peroxide, based upon the weight of the pulp. When hardwoods or other relatively easy to bleach woods are utilized, the peroxide treatment can be conducted by contacting the pulp with amounts of the chemical on the lower end of this range, while softwoods would require greater amounts of chemical which would typically be about 0.3 to 0.5%. The reaction is conducted in a brightening tower 172 for sufficient time to increase the brightness of the pulp to the desired levels. Generally, a GE brightness of about 85 to 93 and preferably above about 90 GEB is attained. The brightness value achieved will depend upon the amounts of chemical used and the brightness of the pulp as it enters into this second peroxide brightening stage.

Preferably, the peroxide step is conducted on pulp having a consistency of about 8 to 35%. The specific peroxide compound to be used, which is generally hydrogen peroxide, as well as the particular stabilizer combinations are considered to be conventional and well within the knowledge of one skilled in the art.

The pulp 180 which exits tower 172 is again thoroughly washed in a washer 182 using fresh water 184. The washed pulp 188 again has a pH near neutral and a

consistency of about 16%. The wash water effluent 166 from this washer 182 can be used to advantage as the washing water for washer 164.

5 The resultant pulp is fully bleached and brightened to GEB values typically of at least about 85 to as high as 93, thus rendering the final product suitable for use as a pulp for making high quality white paper.

10 Other post treatments to stabilize the final brightness, such as SO<sub>2</sub> souring can be employed. The use of such materials is well known to those of ordinary skill in the art and need not be explained in any greater detail here.

#### Examples

15 The scope of the invention is further described in connection with the following examples which are set forth for purposes of illustration only and which are not to be construed as limiting the scope of the invention in any manner. Unless otherwise indicated, all chemical percentages are calculated on the basis of the weight of  
20 OD pulp. Also, one skilled in the art would understand that the target brightness values do not need to be precisely achieved, as GEB values of plus or minus 2% from the target are acceptable.

#### 25 Example 1:

A softwood (pine) pulp was subjected to Kraft AQ pulping followed by an O<sub>m</sub> treatment similar to that of Example 4 of U.S. Patent 5,164,043 to produce a pulp  
30 having a K number of 7.2, a viscosity of 14.3 cps and a brightness of 37% GEB. This pulp was then subjected to ozone delignification and the brightening sequences according to the invention.

35 Since two ozone stages are utilized in the overall process, experiments were conducted to determine whether the charge of the ozone on the pulp in the two ozone



stages significantly affected the final condition of the pulp. In these experiments, a  $Z_m$  stage was conducted on high consistency pulp using paddle reactor 78. An extraction stage was conducted by adding sodium hydroxide to the water in tank 104 to raise the pH of the pulp to about 7.5. The resultant pulp was washed and then subjected to a first peroxide brightening stage. The resultant pulp was then washed and subjected to a second  $Z_m$  stage. Then, the resultant pulp was washed and subjected to a second peroxide brightening stage. The final pulp was then washed and recovered.

Specifically, three experiments were conducted, one in which the ozone charge in the first  $Z_m$  stage was lower than that of the second  $Z_m$  stage, one in which both charges were about the same, and one in which the ozone charge in the first  $Z_m$  stage was higher than that of the second. The  $P_1$  and  $P_2$  conditions were kept the same for all three sequences. The peroxide charge was 0.8% for  $P_1$  and 0.2% for  $P_2$ . Both peroxide stages were conducted at medium consistency. The overall sequence was thus  $Z_{m1}$  E  $P_1$   $Z_{m2}$   $P_2$ , and the brightness and viscosity after each stage was measured. The results appear below in Table 1:

TABLE 1

Experiment	Stage	Charge, %	GEB	K Number	Viscosity cps
1	Z <sub>m1</sub>	0.15	46.1	4.57	13.1
	E	---	45.1	4.15	13.3
	P <sub>1</sub>	0.80	59.5	2.65	10.9
	Z <sub>m2</sub>	0.33	79.1	---	8.0
	P <sub>2</sub>	0.30	81.7	---	8.1
2	Z <sub>m1</sub>	0.26	49.4	3.70	12.2
	E	---	49.7	3.60	12.5
	P <sub>1</sub>	0.80	70.8	---	12.1
	Z <sub>m2</sub>	0.22	80.5	---	9.5
	P <sub>2</sub>	0.30	85.7	---	9.3
3	Z <sub>m1</sub>	0.45	57.0	2.60	11.4
	E	---	59.0	---	11.1
	P <sub>1</sub>	0.80	76.7	---	11.0
	Z <sub>m2</sub>	0.08	81.8	---	9.8
	P <sub>2</sub>	0.30	85.4	---	9.6

The results show that experiments 2 and 3 produced comparable ozone consumption with similar levels of GE brightness values. However, when the initial Z<sub>m</sub> stage used relatively low levels of ozone, the final brightness was found to be significantly lower than that for the other experiments. It was also found that poor selectivity across the first peroxide stage occurred when the lower ozone levels were applied to the first Z<sub>m</sub> stage.

This data demonstrates that the final ozone brightening step should be conducted utilizing the application of the same or lower amount of ozone compared to the initial ozone stage. Since it is known from the disclosure of U.S. Patent 5,164,043 that benefits in the

uniformity of delignification and resultant brightness are achieved when using higher ozone levels by employing a specially designed high consistency ozone stage, it is preferred to utilize the first  $Z_m$  stage for bulk delignification using such higher ozone levels at high consistency.

Example 2:

The process of the invention was conducted on hardwood (Eucalyptus) to illustrate both the chemical requirements and the interstage properties. In this Example, the first  $Z_m$  stage and the first P stage were conducted in the same manner as above in Example 1 except that for the peroxide stage a slightly higher amount of chemical was applied to the pulp. A chelant conditioning stage was conducted by adding DTPA to the pulp in an amount of 0.2% for 1 hour at 90°C, followed by washing. The second Z stage was conducted by introducing medium consistency pulp into a high shear mixer where the ozone was added. The pulp/ozone gas mixture was then allowed to stand in the mixer for completion of the ozone-pulp reaction. Results appear below in Table 2.

TABLE 2

	BROWNSTOCK PULP	
	kappa <sub>10</sub>	12.5
	K <sub>40</sub>	8.4
5	Viscosity, cps	53.3
	O <sub>m</sub> STAGE PULP	
	NaOH, %	2.05
	K <sub>40</sub>	5.5
	Viscosity, cps	26.0
	Z <sub>mi</sub> STAGE PULP	
10	Consistency, %	42%
	O <sub>3</sub> , %	0.37
	GEB %	74.4
	Viscosity, cps	20.7
	Q STAGE PULP	
	Viscosity, cps	20.8
15	P <sub>i</sub> STAGE PULP	
	H <sub>2</sub> O <sub>2</sub> , %	1.0
	GEB %	87.6
	Viscosity, cps	14.9
	Z <sub>m2</sub> STAGE PULP	
	Consistency, %	12
20	O <sub>3</sub> , %	0.11
	GEB %	90.4
	Viscosity, cps	13.6

25 A comparison of the properties of the resultant pulp  
 against those of the same wood species (i.e., Eucalyptus)  
 which was commercially manufactured by a conventional  
 OD/CEDED bleaching sequence is shown below in Table 3.  
 This data illustrates that comparable or slightly  
 improved properties are attained using the process of the  
 30 present invention.

TABLE 3

	<u>Property</u>	<u>Pulp of Example 2</u>	<u>Conventional Pulp</u>
	Brightness, %	90.4	89.4
5	Viscosity, dm <sup>3</sup> /kg	667	665
	Tear Index, Nm <sup>2</sup> /kg	9.0	8.7
	Tensile Index, Nm/Kg	88	77
	Burst, kPAm <sup>2</sup> /g	6.2	5.0
	Stretch, %	5.4	3.5
	Bulk, cm <sup>3</sup> /g	1.4	1.4
	Opacity, %	75	75

10

These data show that a high brightness, good strength hardwood pulp is produced by the process and that this hardwood pulp does not require a second peroxide stage to achieve the high brightness levels which are necessary for high quality white paper production.

15

Example 3

The effect of a second Z stage on Kraft/AQ/O<sub>m</sub> pulps bleached with Z<sub>m1</sub>RQP or Z<sub>m1</sub>R bleaching sequences was investigated. The Kraft/AQ/O<sub>m</sub> pulps were prepared as described above in Example 1. The bulk ozone stage, Z<sub>m1</sub>, consumed 0.55% ozone and produced a pulp of 64.3% GEB. A sodium borohydride reduction treatment used 1% formamidine sulfinic acid ("FAS") at 70°C for 2 hours at 10% consistency to raise the brightness to 70.8% GEB. The Q stage employed 0.2% DTPA at 85°C for 1 hour at 10% consistency. The P stage used 0.6% hydrogen peroxide at 80°C for 5 hours at 10% consistency. 0.25% magnesium sulfate (MgSO<sub>4</sub>) was used as a stabilizer and 0.7% sodium hydroxide was used to adjust the pH. The Z<sub>m1</sub>R(QP) pulp had a final GEB of 83.9%.

The brightness of these pulps entering the second Z stage were significantly different. A graph of GE brightness for several ozone application levels on softwood pulp (a Kraft AQ O<sub>m</sub> Z<sub>m</sub> pine) which was further

35

treated by either a  $R(QP)Z_2$  or  $RZ_2$  sequence is presented in Figure 4. This graph illustrates that the second Z stage is extremely effective at imparting a significant increase in brightness and that the brightness increases can be obtained at relatively low ozone consumption levels. These brightness levels are also larger for the lower brightness pulp. Of course, the final brightness levels are dependent upon the incoming brightness level of the pulp, but significant increases in brightness can be attained over the initial brightness in each instance.

#### Example 4

A softwood (pine) pulp was treated by a Kraft AQ  $O_m$   $Z_m$  E P sequence by methods similar to those of Example 3 to obtain a pulp having a GE brightness of 79.8%. Several treatment steps were applied to this pulp, followed by a second peroxide stage, to determine which would be the most effective brightening sequence.

The treatments that were studied included a second ozonation stage, an acid washing stage and peracid treatment stages using either peracetic or persulfuric acid. A second peroxide stage with only intermediate washing in between the two peroxide stages was conducted as a control.

A summary of the results obtained is shown in Figure 5 as a plot of brightness versus applied peroxide in the second peroxide stage. The acidic treatment stage imparts a small boost to the bleaching sequence. The peracid stages and especially the peracetic acid stage imparts even larger brightness increases. There is, however, only a very marginal brightness increase in the second peroxide stage following the peracetic acid treatment. Although larger brightness increases can be achieved with peracetic acid over persulfuric acid, a reduction in pulp strength as shown by viscosity after this treatment on Kraft pulp also results. This is seen

in Figure 6. In addition, a significant drop in viscosity following the peracetic acid treatment is observed. A second ozone stage in between the two peroxide stages appears to be the best compromise of achieving relatively high brightness without a significant detrimental affect on viscosity.

A second ozonation stage imparts substantial brightness increases both in the ozonation stage and in the peroxide stage that follows. The brightness increase in the second peroxide stage is high even at higher incoming pulp brightness levels. The initial slope at the highest incoming brightness level is comparable to those from all other intermediate treatments. This appears to be related to ozone activation of the pulp to make it more receptive to peroxide bleaching. The chemical requirements for the ozonation stage is also very small, which is why this stage can be conducted either on medium consistency or low consistency pulp. This data shows that the use of an ozone stage between the two peroxide stages provides very high GE brightness in the final product. This result is unexpectedly better than the use of two peroxide treatments or with an intermediate peracid stage, particularly with respect to the GE brightness obtained and the low viscosity loss.

An addition, Figure 5 illustrates the profile of brightness versus applied peroxide for the second P-stage with no intermediate treatment (i.e., the control). The brightness levels reached with successive peroxide stages are not better than with any intermediate treatment case even when high levels of peroxide are applied on pulp. There is a brightness increase from 79.8 after the first peroxide stage to just over 84 after the second peroxide stage. This large brightness increase of just under five points in the second P-Stage is due to the first P-Stage not being near to the plateau level of brightness. Some of the brightness that would otherwise have been obtained

in the first peroxide stage is then being obtained in the second peroxide stage.

Graphs of viscosity versus brightness are shown in Figure 6. A second ozonation treatment as the intermediate stage between peroxide stages results in the best viscosity/brightness relationship. Small ozone applications in the second Z-Stage appear to be advantageous. As noted above, peracetic acid treatment as the intermediate step results in a precipitous drop in the viscosity/brightness relationship.

#### Example 5

To further illustrate the benefits of an intermediate Z-stage between two peroxide treatments, the following tests were conducted.

A comparison of the final peroxide stage on two pulps which were produced by different sequences, but having equal brightness and viscosity, was performed as follows. One pulp was treated by an OZPP sequence, while the other was treated by an OPZP sequence.

Peroxide is selective on the groups of lignin which it can attack, suggesting that the chemical history is important to P-Stage response. Also, peroxide bleaching response differs for pulps of different chemical history. The data presented in Table 6 show that the response to peroxide for softwood (pine) is better after a Z-stage than after a P-stage. The P<sub>2</sub> stage was conducted at 80°C, on 12% consistency pulp for 2 hours, with the application of 1% H<sub>2</sub>O<sub>2</sub> and 0.5%, MgSO<sub>4</sub>.

The optimum conditions for running a P-stage, optimum location for a P-stage, and response for a P-stage will be a function of the chemical history of the pulp. Sequences which include as intermediate Z stage between P stages are preferred for that reason.



TABLE 6

	BEFORE P <sub>2</sub> -STAGE		AFTER P <sub>2</sub> -STAGE	
	GEB, %	VISCOSITY, cps	GEB, %	VISCOSITY, cps
OZP(P <sub>2</sub> )	68.8	9.6	76.7	8.9
OPZ(P <sub>2</sub> )	68.3	9.8	81.0	9.4

Example 6

Figures 7 and 8 illustrate a comparison of the significant GE brightness gains in the second ozone stage with the application of a low level of ozone for pulps made by various bleaching and brightening sequences. Figure 7 is a comparison of softwood (pine) pulp which is initially treated by a Kraft AQ O<sub>m</sub> followed by either a Z<sub>m</sub> E Q P or Z<sub>m</sub> R sequence. The P stage utilized 0.7% hydrogen peroxide. Figure 8 is a comparison of softwood (pine) pulp which is initially treated by a Kraft AQ O<sub>m</sub> followed by either Z<sub>m</sub> R Z<sub>2</sub> or Z<sub>m</sub> R Q P. The P stage utilized 0.6% hydrogen peroxide.

Example 7: Reduction Treatments

Reducing agents such as sodium borohydride (NaBH<sub>4</sub>), formamidine sulfinic acid ("FAS") and sodium hydrosulfite (Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub>) are known to react with colored substituents of lignin to brighten pulp. These agents may also increase the viscosity and strength of ozone treated pulps by reacting with carbonyl groups introduced into carbohydrate chains during ozonation. These carbonyl containing chains can be cleaved in subsequent alkaline stages resulting in weakening of the pulp fibers.

Typical conditions for applying reductive treatments to pulp are shown in Table 7.

TABLE 7

REDUCTIVE BLEACHING AGENTS

5	REACTION	<u>NaBH<sub>4</sub></u>	<u>FAS</u>	<u>Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub></u>
	CONDITIONS			
	% ON PULP	0.1 (0.05)	0.5	1.0
	pH	11.5 STARTING	8.5 STARTING	6 ENDING
	TIME, MIN.	60	60-120	20
10	TEMPERATURE, °C	70	60-70	60
	CONSISTENCY, %	10	10	5-15

The FAS treatment utilized 0.4% FAS and 1% NaOH, for 1.5 hours at 60°C. The results of GE brightness and

15 viscosity versus applied amounts of reduction agent and applied ozone are illustrated in Figures 9-12. Figure 9 shows the effect of FAS and sodium borohydride on Z stage viscosity and brightness for a softwood (southern pine) pulp which has been treated by a Kraft AQ O<sub>m</sub> Z<sub>m</sub> sequence

20 so as to have a viscosity of 9.8 cps and a viscosity of 64.3% GEB. Figure 10 illustrates the effect of sodium hydrosulfite on Z stage viscosity and brightness for a softwood (southern pine) pulp which has been treated by a Kraft AQ O<sub>m</sub> Z<sub>m</sub> sequence so as to have a viscosity of 8.6

25 cps and a viscosity of 53.7% GEB. Figure 11 is a graph of GE brightness versus ozone consumption for Z<sub>m</sub> and Z<sub>m</sub> R treatments which are carried out on a softwood (southern pine) which has been treated by a Kraft AQ O<sub>m</sub> Z<sub>m</sub> sequence. Figure 12 is a graph of viscosity versus ozone

30 consumption for Z<sub>m</sub> and Z<sub>m</sub> R treatments which are carried out on a softwood (southern pine) which has been treated by a Kraft AQ O<sub>m</sub> Z<sub>m</sub> sequence. In each of Figures 11 and 12, the R treatment was carried out at 70°C on 10% consistency pulp for 90 minutes using 1.5% NaBH<sub>4</sub>.

35 These data show that reduction treatments can be used following the first Z<sub>m</sub> stage as a suitable way to

brighten pulp and raise its viscosity prior to a subsequent peroxide stage or a second Z stage.

Example 8:

A mill southern pine was obtained after the O stage. This pulp was made by a modified Kraft cooking procedure and a conventional high consistency O stage and possessed a K No. of 8.1 and a viscosity of 13.7 cps. This pulp was then further delignified and bleached using (1)  $Z_{m1}$  QPZ<sub>2</sub> and (2)  $Z_{m1}$  QP<sub>1</sub>Z<sub>2</sub>P<sub>2</sub> sequences. The conditions employed are shown below in Table 8. The chemical charges employed and the results obtained in each stage are shown below in Table 9. The  $Z_{m1}$  QPZ<sub>2</sub> sequence produced a southern pine pulp of 85.2% GEB at a viscosity of 9.1 cps, while employing a total of 0.66% ozone and a total of 0.7% hydrogen peroxide. The  $Z_{m1}$  QP<sub>1</sub>Z<sub>2</sub>P<sub>2</sub> sequence produced a pulp of 89.3% GEB at a viscosity of 9.0 cps employing a total of 0.66% ozone and a total of 0.95% hydrogen peroxide.

Table 8

Reaction Conditions				
Stage	Consistency (%)	Time (min.)	Temperature (°C)	pH
$Z_m$	42	2	25	2
Q	10	60	90	7.5
P <sub>1</sub>	10	180	80	10.5
Z <sub>2</sub>	12	1.5	25	2
P <sub>2</sub>	10	120	80	10.5

Table 9SOUTHERN PINE BLEACHING RESULTS

Starting Pulp: modified Kraft/O, K No. 8.1, viscosity  
13.7 cps

	<u>Stage</u>	<u>Z<sub>ml</sub> OPZ<sub>2</sub></u>	<u>Z<sub>ml</sub> OP<sub>1</sub>Z<sub>2</sub>P<sub>2</sub></u>
5	Z <sub>ml</sub>		
	ozone, %	0.52	0.52
	GEB, %	61.5	61.5
10	viscosity, cps	10.3	10.3
	Q		
	DTPA, %	0.2	0.2
	viscosity, cps	10.9	10.9
15	GEB, %	61.6	61.6
	P <sub>1</sub>		
	H <sub>2</sub> O <sub>2</sub> , %	0.7	0.7
	MgSO <sub>4</sub> , %	0.25	0.25
	NaOH, %	0.7	0.7
20	GEB, %	79.4	79.4
	viscosity, cps	10.6	10.6
	Z <sub>2</sub>		
	ozone, %	0.14	0.14
	GEB, %	85.2	85.2
25	viscosity, cps	9.1	9.1
	P <sub>2</sub>		
	H <sub>2</sub> O <sub>2</sub> , %	-	0.25
	MgSO <sub>4</sub> , %	-	0.25
	NaOH, %	-	0.7
30	GEB, %	-	89.2
	viscosity, cps	-	9.0

These tests demonstrate that southern pine can be  
treated as disclosed herein to produce a pulp of good  
viscosity and high brightness with reasonable bleach  
changes.

THE CLAIMS

What is claimed is:

1. A process for the manufacture of a bleached pulp having a certain brightness and a certain strength  
5 as indicated by a certain viscosity which comprises:

chemically digesting a lignocellulosic material to initially form a pulp;

10 oxygen delignifying the pulp to remove a substantial portion of the lignin therefrom, with the combination of the digesting and oxygen delignifying steps being conducted to form an intermediate pulp having a specified amount of lignin and a specified viscosity;

15 ozone delignifying the intermediate pulp with a gaseous mixture that contains ozone by adjusting the pH of the pulp to below about 4, adjusting the consistency of the pulp to a high consistency of above about 20%, and treating the pulp with an amount of the ozone containing gaseous mixture sufficient to remove a substantial  
20 portion, but not all, of the remaining lignin by intimately contacting and turbulently mixing the pulp particles with the gaseous mixture in a dynamic reaction zone for a sufficient time and at a temperature sufficient to allow access of the ozone to substantially  
25 all of the pulp for reaction therewith while the pulp advances through substantially all of the reaction zone, thus obtaining substantially uniform delignification of a significant portion of the pulp and forming a delignified pulp having a reduced amount of lignin and the certain strength, viscosity and brightness;

30 wherein the specified amount of lignin of the intermediate pulp is such that, after ozone delignification, the delignified pulp attains the certain GE brightness, and wherein the specified viscosity of the intermediate pulp is sufficiently high to permit the  
35 delignified pulp, after ozone delignification, to attain

the certain strength as evidenced by the certain viscosity; and

increasing the certain brightness of the delignified pulp by subjecting the pulp to a brightening sequence which comprises:

5           treating the delignified pulp with a peroxide compound under conditions sufficient to raise the certain brightness of the pulp to a first increased brightness which is higher than the certain brightness; and

10           subsequently treating the pulp with ozone under conditions sufficient to raise the first increased brightness of the pulp to a second increased brightness which is higher than the first increased brightness.

2.   The process of claim 1 wherein the peroxide treatment comprises increasing the pH of the pulp to at  
15   least about 9, treating the pulp with a peroxide stabilizing agent and contacting the pulp with a sufficient amount of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the first increased brightness.

20   3.   The process of claim 2 wherein the peroxide treatment comprises providing the consistency of the delignified pulp at between about 8-35%, increasing the pH of the pulp to between about 9.5 and about 11.5, treating the pulp with a peroxide stabilizing agent and  
25   contacting the pulp with between about 0.2 and 2% by weight based on the oven dry weight of the pulp of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the first increased brightness.

30   4.   The process of claim 1 wherein the ozone brightening treatment comprises reducing the pH of the peroxide treated pulp to less than about 7 and contacting the pulp at a consistency of about 1-18% with a  
35   sufficient amount of ozone to achieve the second increased brightness.

5. The process of claim 3 wherein the ozone brightening treatment comprises reducing the pH of the peroxide treated pulp to less than about 4 and contacting the pulp at a consistency of about 5-15% with an amount of ozone of between about 0.01 and 0.5% by weight based on the oven dry weight of the pulp to achieve the second increased brightness.

6. The process of claim 1 wherein the brightening sequence further comprises subsequently treating the ozone brightened pulp with a peroxide compound under conditions sufficient to raise the second increased brightness of the pulp to a third increased brightness which is higher than the second increased brightness.

7. The process of claim 6 wherein the subsequent peroxide treatment comprises increasing the pH of the pulp to at least about 9 and contacting the pulp with a sufficient amount of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the third increased brightness.

8. The process of claim 6 wherein the subsequent peroxide treatment comprises providing the consistency of the ozone brightened pulp at between about 8-35%, increasing the pH of the pulp to between about 9.5 and about 11.5 and contacting the pulp with between about 0.1 and 4% by weight based on the oven dry weight of the pulp of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the third increased brightness.

9. The process of claim 8 wherein the amount of peroxide compound used in the subsequent peroxide treatment step is between about 0.2 and 0.5% and which further comprises treating the pulp with a peroxide stabilizing agent prior to conducting the subsequent peroxide treatment.

10. The process of claim 6 wherein the pulp is washed between brightening treatments, and the certain

brightness is between about 48 and 80 GEB, the first increased brightness is between about 65 and 90 GEB and is increased by at least about 10 to 20 GEB over that of the certain brightness, the second increased brightness is between about 78 and 92 GEB and is increased by at least about 2 to 13 GEB over that of the first increased brightness, the third increased brightness is between about 83 and 93 GEB and is increased by at least about 1 to 5 GEB over that of the second increased brightness.

11. The process of claim 1 which further comprises conducting an alkaline extraction on the pulp after the ozone delignifying step.

12. The process of claim 11 wherein the alkaline extraction step is conducted by contacting the pulp with a solution of an alkaline material for a sufficient time and at a sufficient temperature to solubilize a substantial portion of any lignin which remains in the pulp prior to the brightening sequence.

13. The process of claim 11 which further comprises treating the pulp with an additive to prevent loss of viscosity during the extraction treatment.

14. The process of claim 13 wherein the additive is sodium borohydride, formamidine sulfinic acid or sodium hydrosulfite

15. A process for the manufacture of a bleached pulp having a certain brightness and a certain strength as indicated by a certain viscosity which comprises:

chemically digesting a lignocellulosic material to form a pulp;

oxygen delignifying the pulp by:

applying a first amount of alkaline material to brownstock pulp having a low consistency of less than about 5% by weight by combining the low consistency pulp with a sufficient quantity of alkaline material with uninterrupted mixing in a manner to ensure that all pulp fibers are exposed to the alkaline material to obtain a



substantially uniform distribution of alkaline material throughout the pulp and then increasing the consistency of the alkaline material containing pulp to at least about 18% by weight to obtain high consistency pulp and to remove liquid while retaining the first amount of alkaline material substantially uniformly distributed throughout the high consistency pulp, said pulp fibers containing the alkaline material being directly passed from the combining step to the consistency increasing step;

applying a second amount of alkaline material onto the high consistency pulp to obtain a total amount of alkaline material on the pulp of at least about 0.8 to 7 percent by weight based on the oven dry weight of the pulp, wherein at least about 55% of the total amount of alkaline material is applied to the pulp during the alkaline material combining step; and

subjecting the increased consistency alkaline material containing pulp to high consistency oxygen delignification to obtain enhanced delignification of the pulp without a corresponding decrease in pulp viscosity compared to pulp which is not combined with alkaline material at low consistencies and form an intermediate pulp having a specified amount of lignin and having a specified viscosity;

ozone delignifying said intermediate pulp with an effective amount of ozone for a sufficient time to obtain a delignified pulp having a reduced amount of lignin and the certain GE brightness, strength and viscosity;

wherein the specified amount of lignin of the intermediate pulp is such that, after ozone delignification, the delignified pulp attains the certain brightness, and wherein the specified viscosity of the intermediate pulp is sufficiently high to compensate for viscosity decreases during ozone delignification, thus

permitting the delignified pulp to attain the certain strength as evidenced by the certain viscosity; and increasing the brightness of the substantially delignified pulp by subjecting the pulp to a brightening sequence which comprises:

5           treating the delignified pulp with a peroxide compound under conditions sufficient to raise the certain brightness of the pulp to a first increased brightness which is higher than the certain brightness; and

10           subsequently treating the pulp with ozone under conditions sufficient to raise the first increased brightness of the pulp to a second increased brightness which is higher than the first increased brightness.

15           16. The process of claim 15 wherein the peroxide treatment comprises increasing the pH of the pulp to at least about 9, treating the pulp with a peroxide stabilizing agent and contacting the pulp with a sufficient amount of a peroxide compound at a sufficient  
20           temperature and for a sufficient time to achieve the first increased brightness.

          17. The process of claim 16 wherein the peroxide treatment comprises providing the consistency of the delignified pulp at between about 8-35%, increasing the  
25           pH of the pulp to between about 9.5 and about 11.5, treating the pulp with a peroxide stabilizing agent and contacting the pulp with between about 0.2 and 2% by weight based on the oven dry weight of the pulp of a peroxide compound at a sufficient temperature and for a  
30           sufficient time to achieve the first increased brightness.

          18. The process of claim 15 wherein the ozone brightening treatment comprises reducing the pH of the peroxide treated pulp to less than about 7 and contacting  
35           the pulp at a consistency of about 1-18% with a

sufficient amount of ozone to achieve the second increased brightness.

19. The process of claim 15 wherein the ozone brightening treatment comprises reducing the pH of the peroxide treated pulp to less than about 4 and contacting the pulp at a consistency of about 5-15% with an amount of ozone of between about 0.01 and 0.5% by weight based on the oven dry weight of the pulp to achieve the second increased brightness.

20. The process of claim 15 wherein the brightening sequence further comprises subsequently treating the ozone brightened pulp with a peroxide compound under conditions sufficient to raise the second increased brightness of the pulp to a third increased brightness which is higher than the second increased brightness.

21. The process of claim 20 wherein the subsequent peroxide treatment comprises increasing the pH of the pulp to at least about 9 and contacting the pulp with a sufficient amount of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the third increased brightness.

22. The process of claim 21 wherein the subsequent peroxide treatment comprises providing the consistency of the ozone brightened pulp at between about 8-35%, increasing the pH of the pulp to between about 9.5 and about 11.5 and contacting the pulp with between about 0.1 and 4% by weight based on the oven dry weight of the pulp of a peroxide compound at a sufficient temperature and for a sufficient time to achieve the third increased brightness.

23. The process of claim 22 wherein the amount of peroxide compound used in the subsequent peroxide treatment step is between about 0.2 and 0.5% and which further comprises treating the pulp with a peroxide stabilizing agent prior to conducting the subsequent peroxide treatment.

24. The process of claim 20 wherein the pulp is washed between brightening treatments, and the certain brightness is between about 48 and 80 GEB, the first increased brightness is between about 65 and 90 GEB and is increased by at least about 10 to 20 GEB over that of the certain brightness, the second increased brightness is between about 78 and 92 GEB and is increased by at least about 2 to 13 GEB over that of the first increased brightness, the third increased brightness is between about 83 and 93 GEB and is increased by at least about 1 to 5 GEB over that of the second increased brightness.

25. The process of claim 15 which further comprises conducting an alkaline extraction on the pulp after the ozone delignifying step.

26. The process of claim 25 wherein the alkaline extraction step is conducted by contacting the pulp with a solution of an alkaline material for a sufficient time and at a sufficient temperature to solubilize a substantial portion of any lignin which remains in the pulp prior to the brightening sequence.

27. The process of claim 25 which further comprises treating the pulp with an additive to prevent loss of viscosity during the extraction treatment.

28. The process of claim 27 wherein the additive is sodium borohydride, formamidine sulfinic acid or sodium hydrosulfite

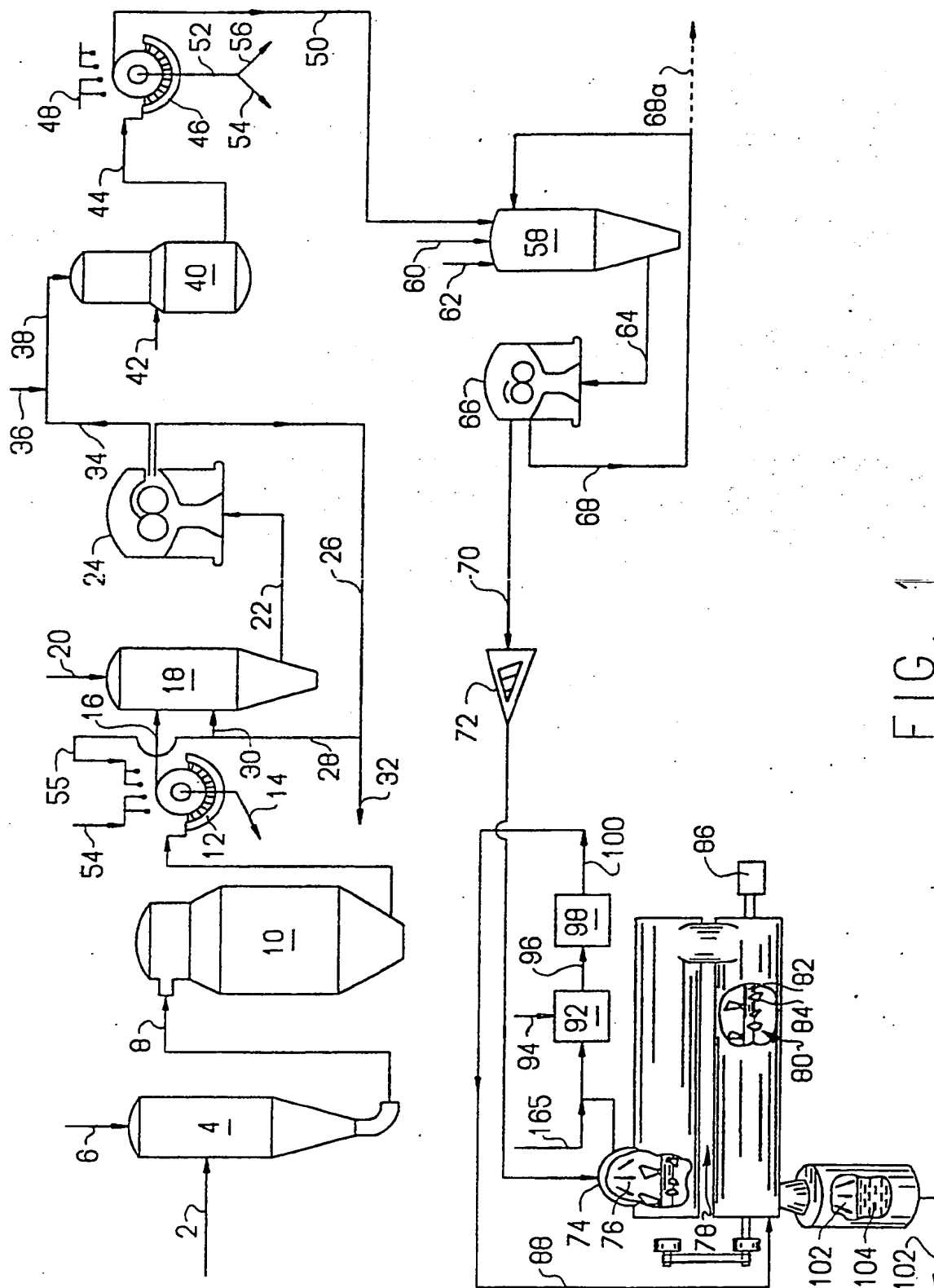


FIG. 1

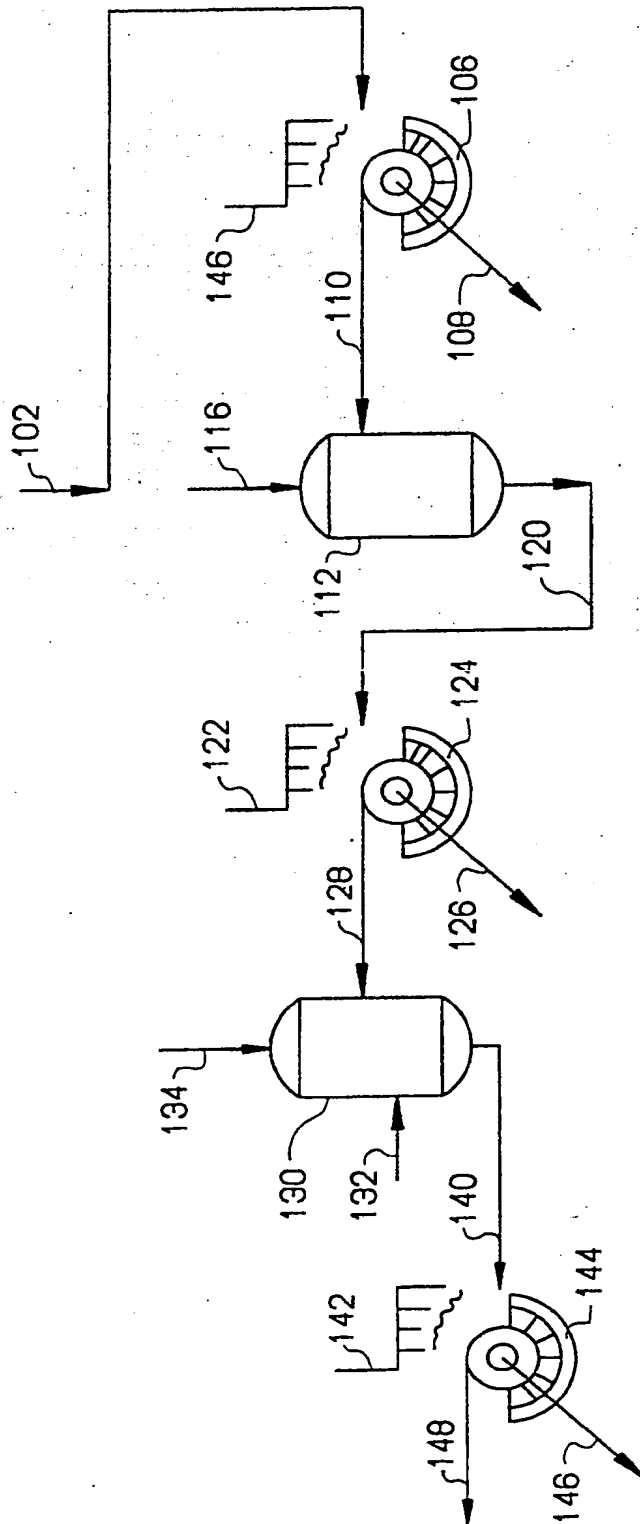


FIG. 2

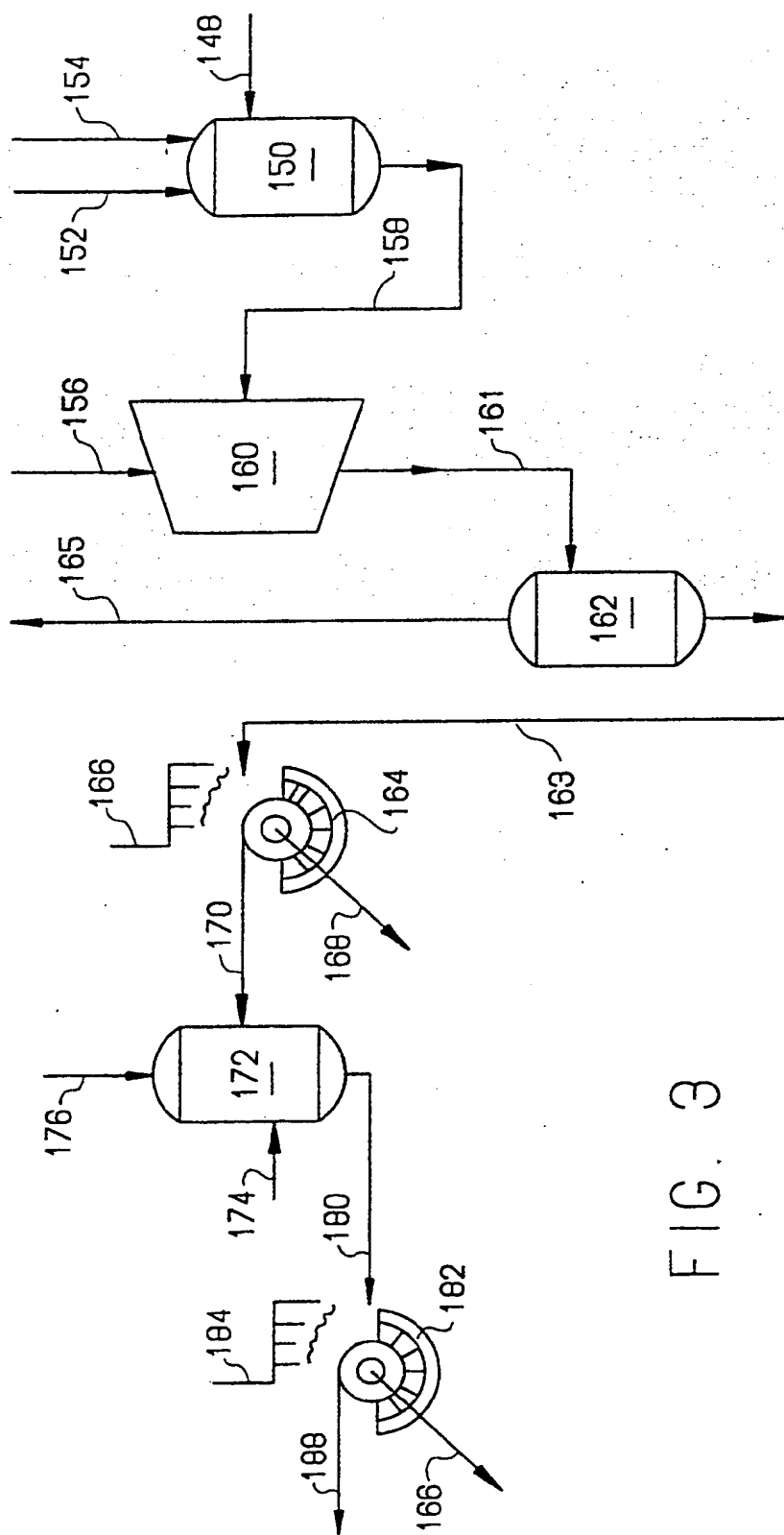


FIG. 3

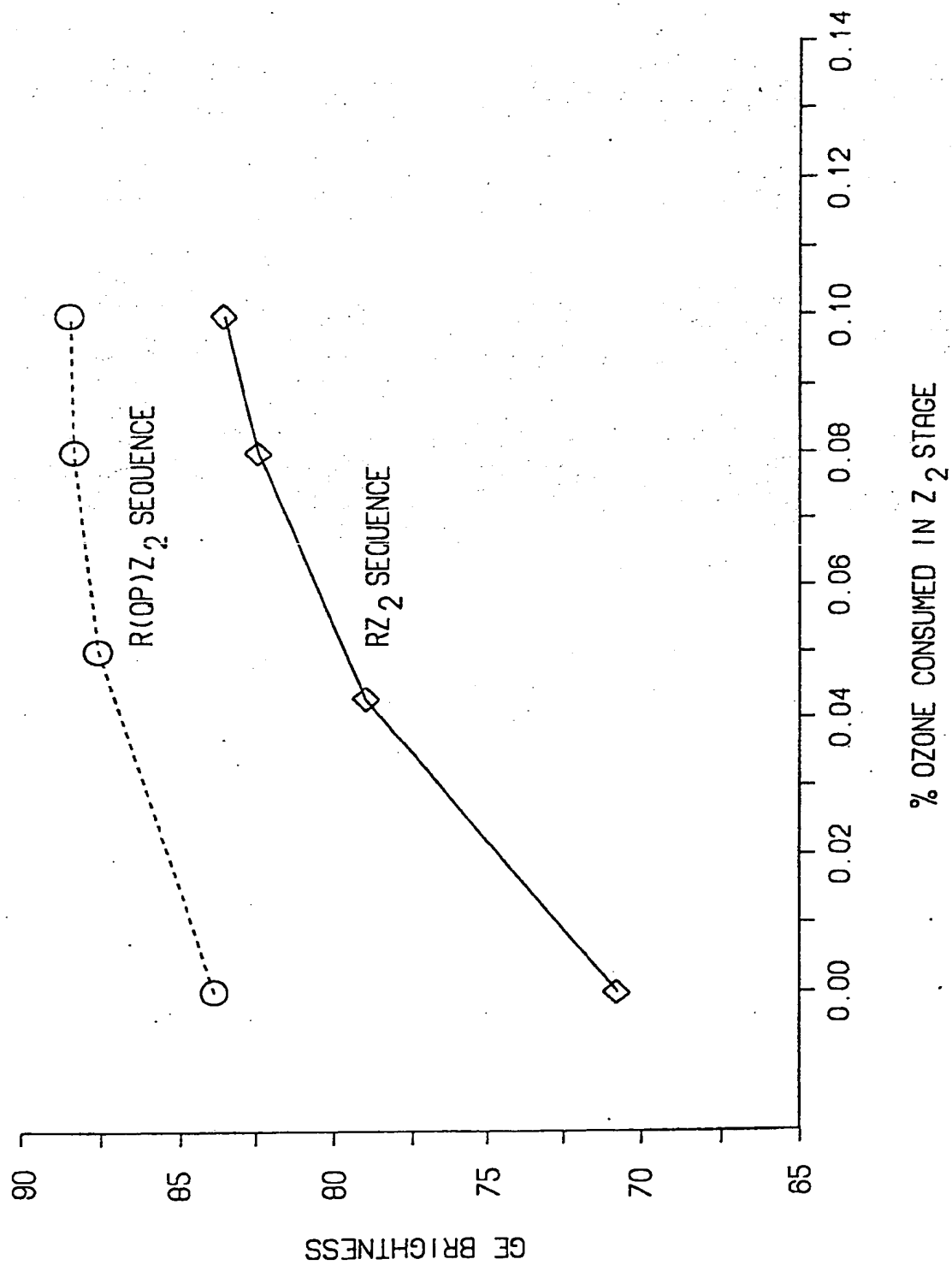


FIG. 4



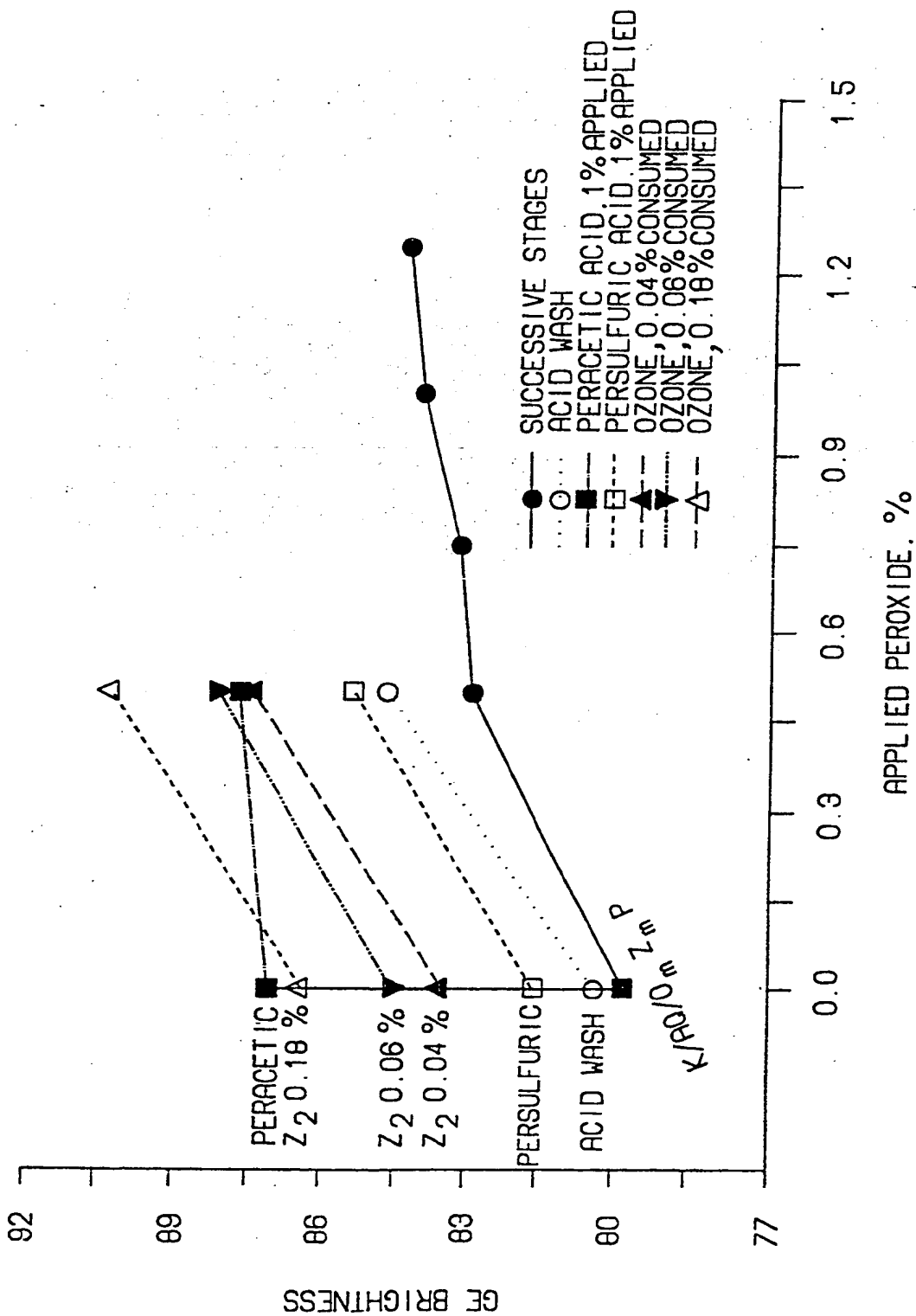
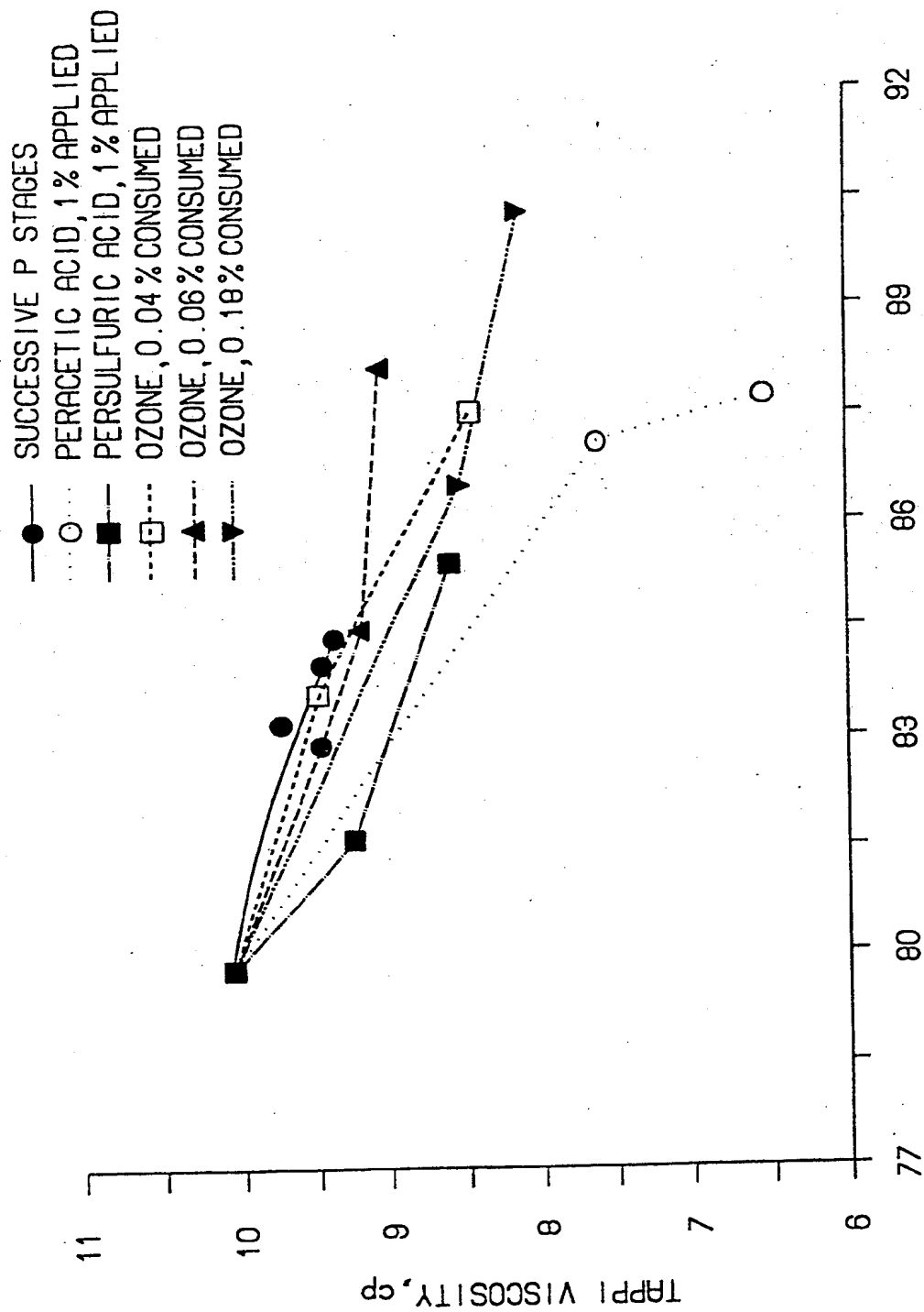


FIG. 5



GE BRIGHTNESS

FIG. 6

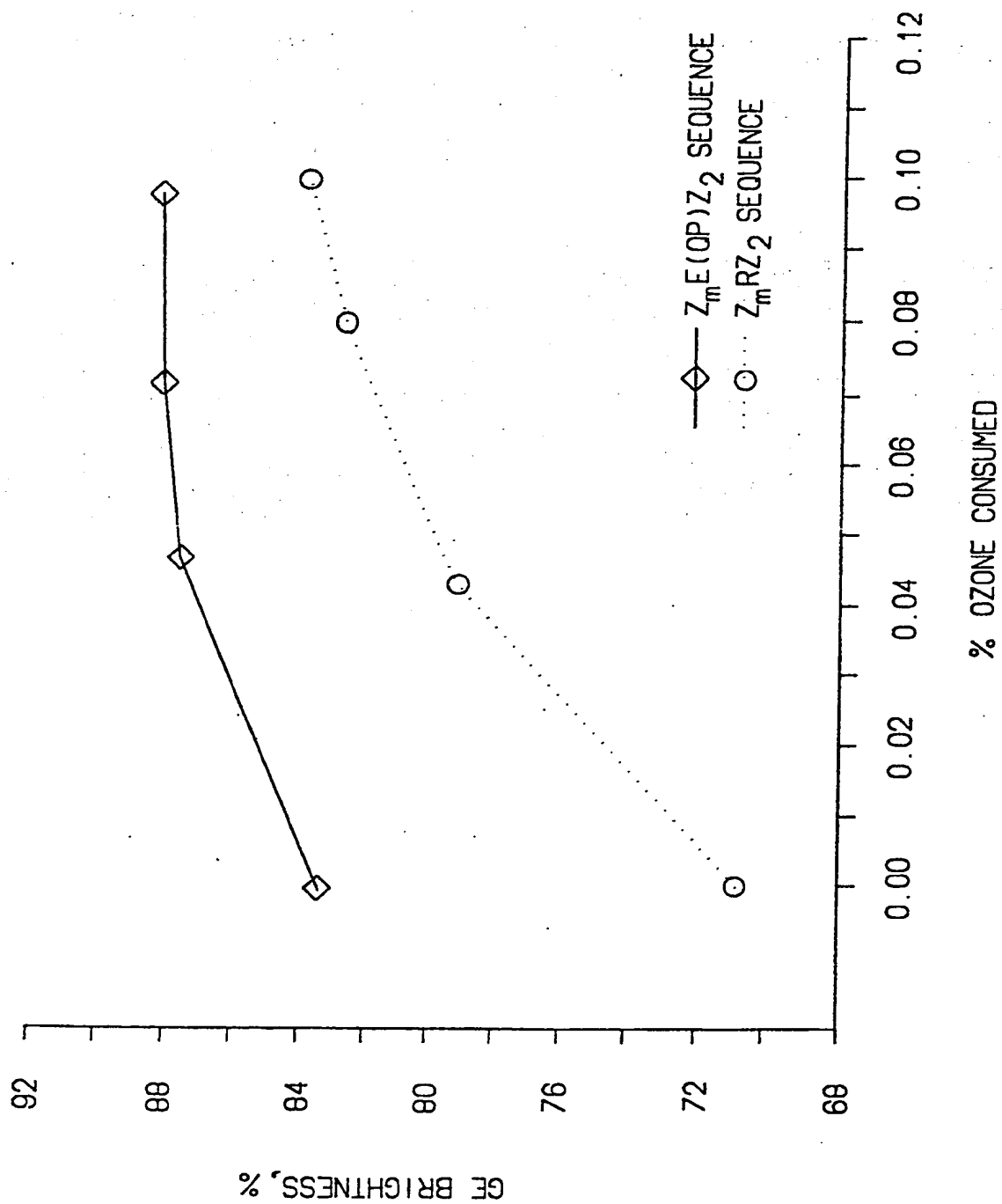


FIG. 7

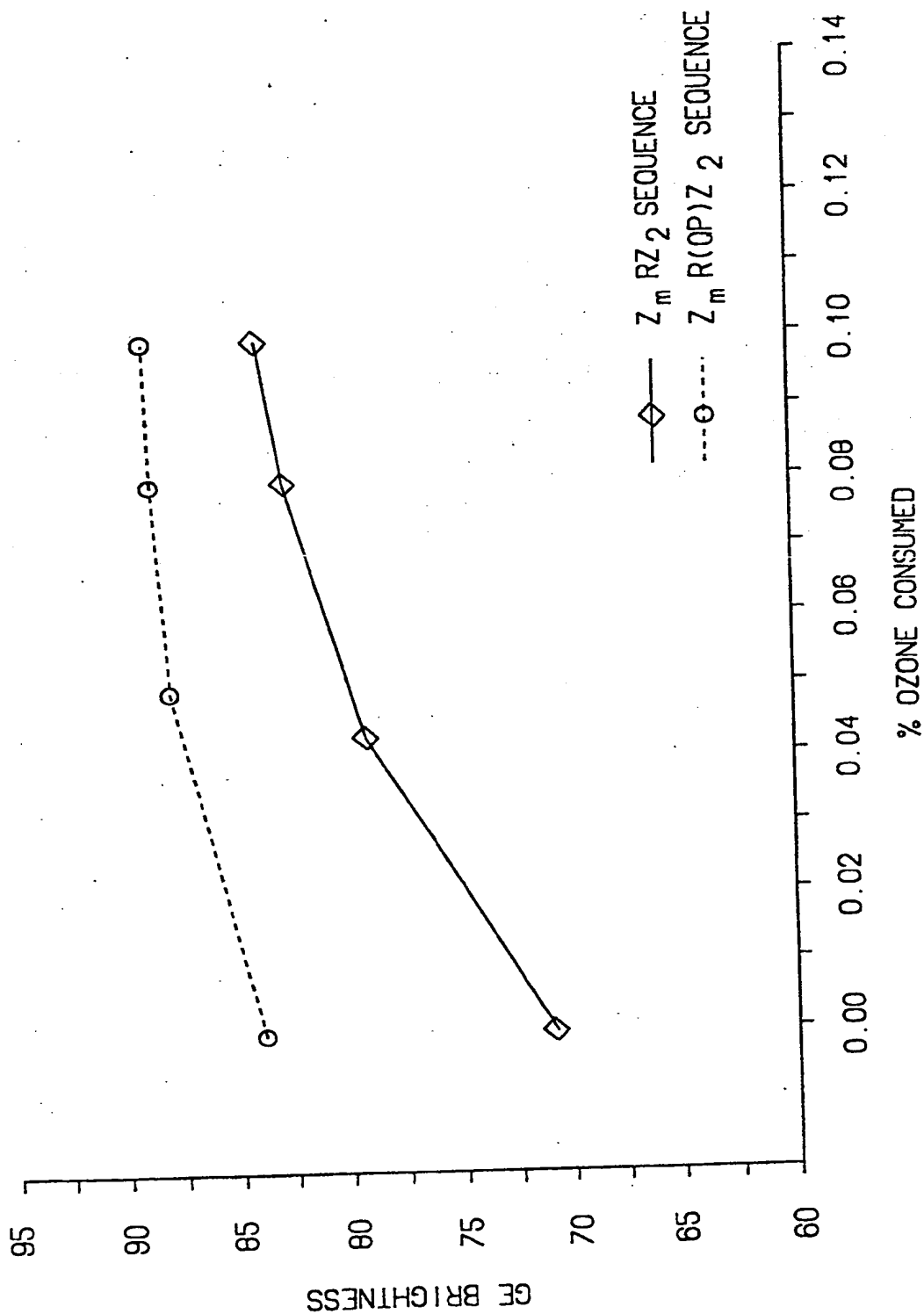


FIG. 8

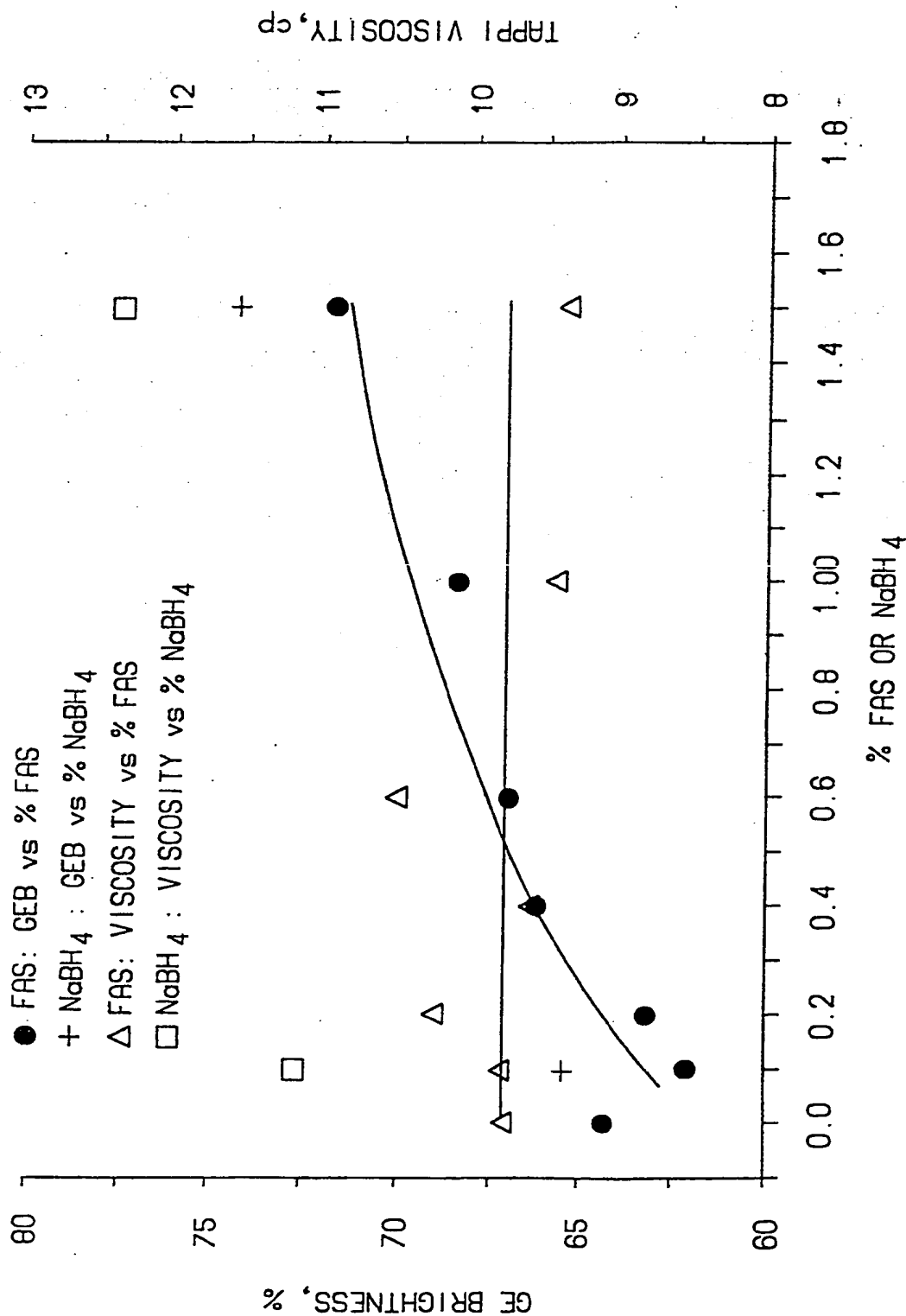


FIG. 9

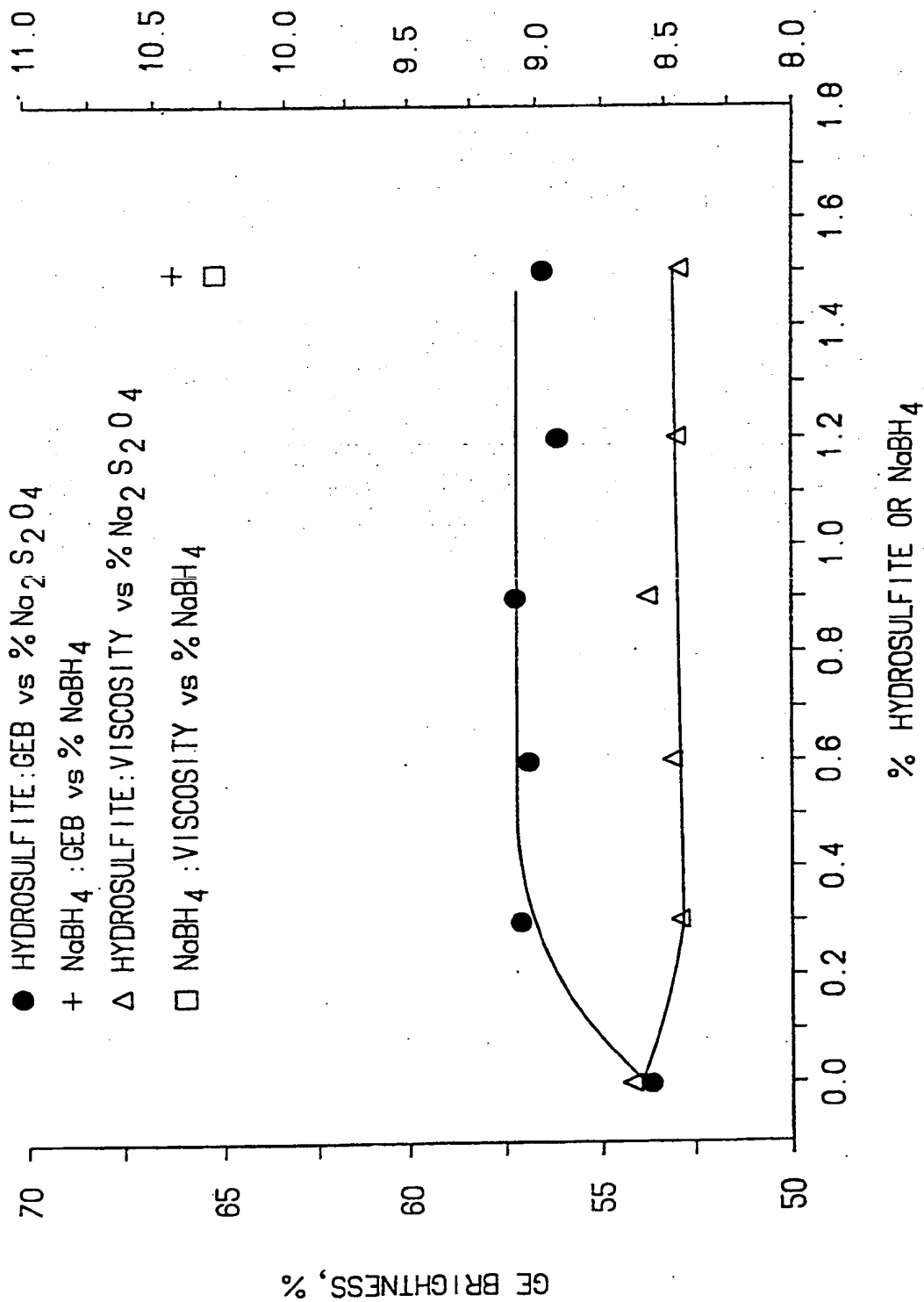


FIG. 10

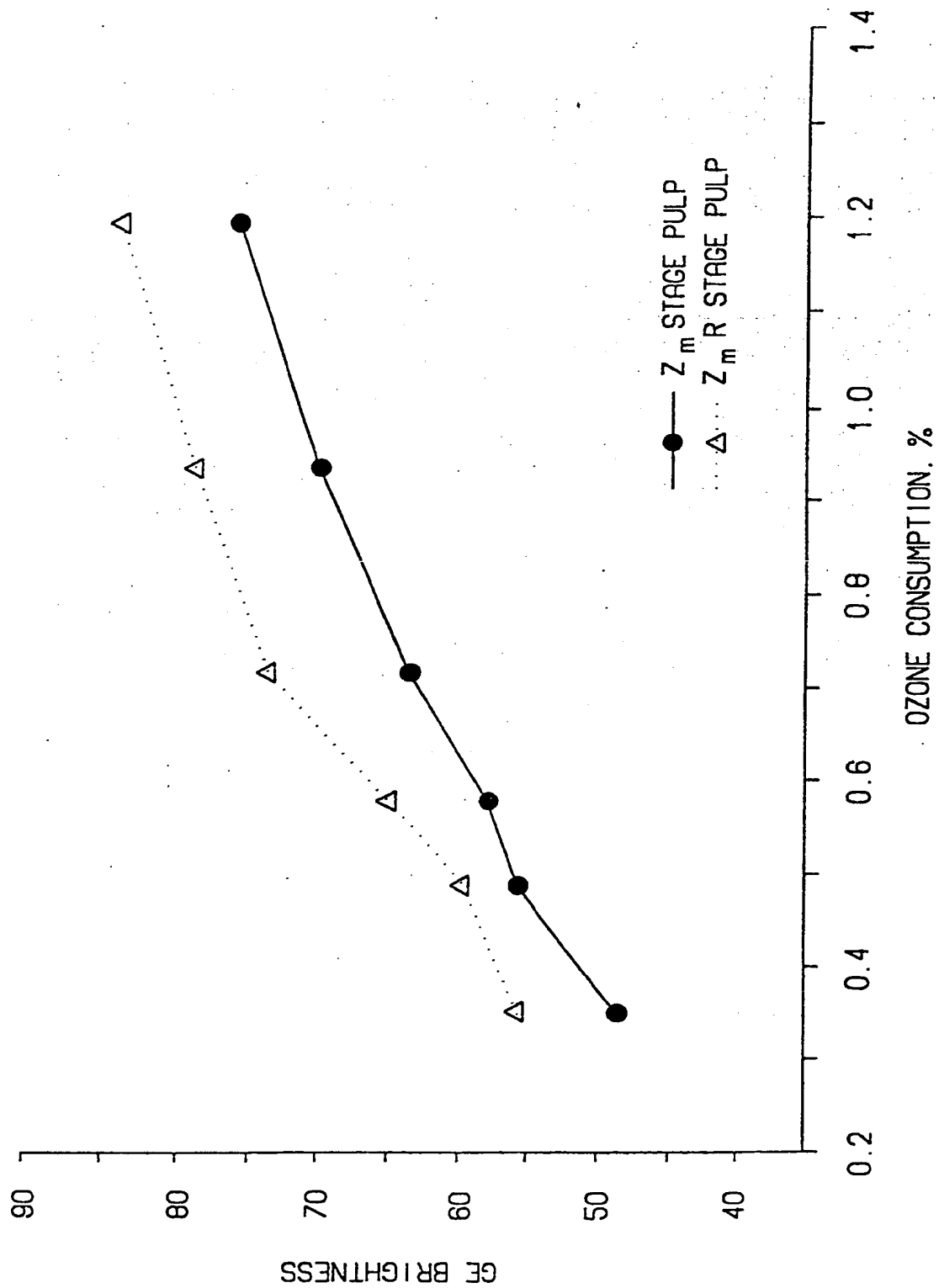


FIG. 11

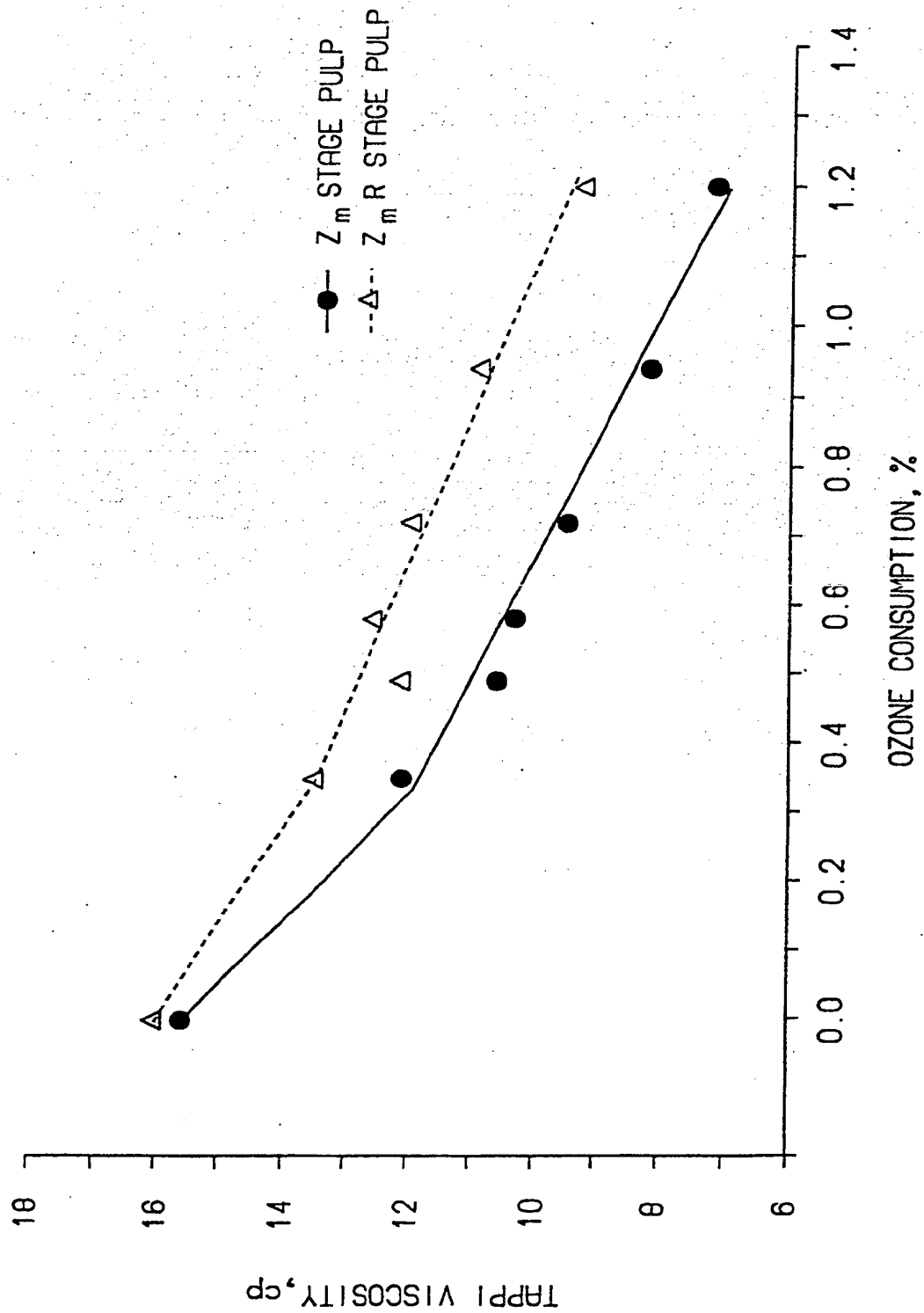


FIG. 12



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/10050

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :D21C 9/153, 9/16

US CL :162/57, 65, 78, 90

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 162/19, 57, 65, 76, 78, 90

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
NONE

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
NONE

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US, A, 5,173,153 (TERRET ET AL) 22 December 1992, See column 4, lines 56-60 and column 5, lines 50-53.	15-28
X,P	US, A, 5,310,458 (LUNDGREN ET AL) 10 May 1994, See Abstract.	2, 3, 5, 7-9, 16, 17 and 21-23
X,P	US, A, 5,328, 564 (GREENWOOD ET AL) 12 July 1994, see Figure 1.	1-28
X	WO, A, 91/18145 (GRIGGS ET AL) 28 November 1991, see Abstract.	1-28
X	Int. Pulp Bleaching Conference, June 11-14 1991, MACAS ET AL, "Production of Bleached Chemical Pulp in the Future", pages 1-16, especially page 4, paragraph 4.	1-28



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	* T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
* A* document defining the general state of the art which is not considered to be part of particular relevance	* X	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
* E* earlier document published on or after the international filing date	* Y	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
* L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* &	document member of the same patent family
* O* document referring to an oral disclosure, use, exhibition or other means		
* P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search

01 NOVEMBER 1994

Date of mailing of the international search report

05 DEC 1994

Name and mailing address of the ISA/US  
Commissioner of Patents and Trademarks  
Box PCT  
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

STEVE ALVO

Telephone No. (703) 308-2048

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US94/10050

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	Journal of Pulp and Paper Science, Volume 19, No. 3, issues May 1993, LINDHOLM, "Alkaline Extraction of Ozone Bleached Pulp" pages 108-113, especially page 108, column 2, lines 10-25.	13, 14, 27 and 28